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American General Education Series

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American General Education Series

Under the Editorship of Malcolm S. MacLean Hampton Institute

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A PRACTICAL SURVEY OF CHEMISTRY WALTER S. DYER

A PRACTICAL SURVEY OF CHEMISTRY

WALTER S. DYER
UNIVERSITY OF ARKANSAS



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EDITOR'S PREFACE

In the present moment of world conflict and far-flung struggle over political philosophies and ways of life, science, especially physical science, has shown its greatest magnification of importance. The man in the street, the high school and college student argue the merits of air-cooled and liquid-cooled bomber and fighter engines. They talk with some knowledge of blitzkriegs and mechanized divisions; of delayed, demolition, and incendiary bombs; of concentrated vitamins in pellet, liquid, or dried food forms for the starving moppets thrown up as flotsam and jetsam by the backwash of war. They discuss the rapid healing of shrapnel and machine gun wounds by treatment with sulfanilamide and sealed, light plaster casts as well as oxygen therapy by means of BLB rubber masks originally designed to prevent plane blackouts in a flyer's plunge from high to low altitudes, and now employed to relieve shock of civilian victims.

In the United States we move all-out for total national defense and deal in our daily talks with plastic planes and bombsights, with wind tunnels and new explosives, with a vast new field of chemistry applied to medicine and healing, with better housing and nutrition for all our people that they may be strong against whatever comes.

In the face of this vastly heightened and intensified interest in the physical sciences, Dr. Dyer's book is most timely. It is by no means restricted to some of the reprehensible activities of mankind which we hope represent a passing phase. It gives, with clarity, scientific background and illumination to many hundreds of problems of universal interest.

It goes further. It is one of the first books in the field of the

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physical sciences in general education which offers a sound basis to the student, who is not to become a chemist, for learning in the classroom and through reading a valid lay knowledge of the field and a layman's appreciation of it; of its importance in the daily life of all the people all the time. It is a fresh book; not an imitation of the long line of chemistry texts issuing out of the early nature study and natural history courses in American education but one which, rather, approaches the field of chemistry with a sense of what students really want to know about the field to their own profit. It is the first, but by no means the final answer to the several questions raised by many teachers and institutions over the past 20 years as to the place of chemistry in general and liberal education, as to materials to be covered in an orientation or survey course with or without subsidiary laboratories, and as to the method whereby chemistry might be so written and so taught that it would not leave a shambles of many good students who "flunked the course" because they "couldn't do science." Dr. Dyer's book, on the contrary, well taught and well studied in courses in general education, will unquestionably have the effect of diminishing the blindness and resistance of nonscience students to this study; and it should increase in great numbers those who both understand and want more of chemistry.

MALCOLM S. MACLEAN

Hampton Institute January 16, 1941

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PREFACE

In writing this practical survey of Chemistry the author has attempted to follow a course of logical development. Since it is intended for students who are not specializing in Chemistry, an obvious effort here has been made to group the discussion around the chemical substances commonly known and used. There has been no thought of offering preparation for a chemical career but constant attention has been given to the business of understanding the things with which chemistry deals.

The material presented here follows, with few exceptions, the basic outline dealing with the cultural side of chemistry, which the author has used in classes since 1926. This particular information may not fit the needs of every teacher who attempts to lead a class in a survey course but it is hoped that

enough suggestions are given to make his task easier.

Expressions of gratitude are due to Professor A. L. Vaughan, of the University of Minnesota, who has given freely of his time and efforts to read the manuscript and offer suggestions, as well as to give needed encouragement; to Professors Hale, Humphreys, and McLain of the University of Arkansas who have read the manuscript and given valuable criticisms; and to the many firms who have so kindly contributed the photographs used throughout the text.

W. S. D.

Fayetteville, Arkansas December, 1940



Chapter 1

INTRODUCTION

The Field of Chemistry. To the man on the street chemistry is just another science which he takes for granted. Sometimes he says, "Isn't it wonderful?" as he reads about the so-called marvels of science in his fat Sunday newspaper which displays in vivid words and pictures the spectacular and the fantastic in chemistry. Much of this material is, of course, a sort of chemistry; but such articles are usually quite different from an authentic report on the progress of science. Within the past fifteen years, however, we have had increasingly better treatment of science for laymen. Many books have been written about the work of chemistry and about the great things which have been accomplished through the application of chemical ideas to serve us all in our daily life. Many of these books are sound and well written. They are intended for the nonscientific reader and naturally do not try to explain the fundamentals of the science as a student must have them explained.

It is common knowledge that chemistry plays a large part in the production of useful things and that men and women trained in the science have contributed to many of our comforts of life. Materials to build homes, offices and factories, as well as cars and other useful things: materials such as steel, alloys, glass, Portland cement, insulation, synthetic plastics, and surface coatings such as paint are products directly resulting from the work of the chemist. It is not at all difficult to see the enormous number of uses to which such substances are put in the modern way of doing things. Our high-speed transportation systems would be impossible without these new materials of construction, and without the proper fuels to supply the required energy. Speedliners as well as the rails they run

on, the engines that drive them, and the fuels and lubricants they use — all come out of chemistry. The largest transport planes are able to carry heavier loads because they use special gasolines in getting off of the ground and these are produced entirely by chemical methods. One has also only to try to imagine the world without modern explosives which have blasted out hills, clay and rocks to clear the way for our many miles of beautiful highways, or have made possible the enormous dams which the government has built to furnish power and irrigation the country over. Such useful explosives, as well as those which help to rain death from the skies, have been made possible by the chemist.

Recently the chemist has turned his attention increasingly to the production, conservation, and utilization of foods. In many sections of the world the farms have worn out, been drained of their chemical plant foods. The day when a farmer could use up his soil and then move on to new and more fertile land has passed. Therefore by planned study and experiment the scientists have discovered requirements for plant growth, and one by one these requirements are being met by fertilization. When the necessary substances are not found in nature in suitable form to package, ship and spread on the land, the chemist is again called upon to convert things that do occur in nature into usable material. Notable examples of this may be found in the production of nitrogen compounds from the nitrogen of the air and the production of soluble phosphate fertilizers from the insoluble rock phosphates which occur in the earth.

The need for proper preservation of food for long keeping or shipping has brought about the modern mechanical refrigerator which uses refrigerants manufactured by chemists. Indeed, the refrigerant which usually is considered as the most efficient and the safest of all those used was actually made to order in a chemical laboratory. The tin can, too, has been elevated to a position of importance. By careful study and planned experiment this method of food preservation has made possible a uniform supply of food throughout the year



Fig. 1. Chemistry Controls Glass Production

The "batch" must be kept at high chemical purity in order to produce glass which will pass rigid inspection. This photograph shows scientists at work in the Libbey-Owens-Ford Glass Company laboratory in Toledo, Ohio.

which is almost entirely free from the dangers encountered only a few years ago.

One of the most interesting fields of study and experiment has to do with the body processes. Each year we learn more about how our body works and why it stops working. In this new knowledge the function of the food we eat has taken on a tremendous importance. We now have available considerable information on the nature and the cause of disease and in some instances specific remedies have been produced which

will probably bring about the complete eradication of some of our most dreaded ailments. Thus the chemically produced vitamins are protecting and building health while new chemical drugs like sulfanilamide help to cure some old and formerly stubborn diseases and one of its near relatives, sulfapyridine, is making some types of pneumonia less deadly.

We also owe much to those chemists who serve as watchdogs over things we buy and use every day. Some of these are employed by the producers in order that they may make us a better product. Others are hired by the government to enforce minimum standards of value, purity, and stability. In other cases we are constantly indebted to them as chemists for

helping to make possible a more abundant life.

It is not intended to give the impression that all chemists are busy making practical things or that in their laboratories and studies they reject all things whose uses are not at once apparent. This is far from the actual truth. Man's knowledge is never so far advanced that he can at once determine whether a new thing is useful in one or many ways. He must first learn all that he can about a new substance. Many times, moreover, the chemist himself fails to see any use for the thing he has studied, but he does take the time to make a careful record of what he has learned. Frequently the person of practical mind who knows little chemistry reads the chemist's report. Sensitive to what we want or to what the manufacturers are looking for, he makes the application of the new knowledge. Thus new industries spring up and the seemingly useless labor of the chemist becomes translated into human value.

The way in which a chemist or anyone else learns about things is sometimes complex and hard to follow. The method he employs will depend upon what he wants to find out as well as upon his individual interests. We have examples of such diversity all about us. Let us imagine a group of people looking at an oil painting which is surrounded by a frame of beautiful wood. We know that many persons will be concerned only with the artistic effect produced. On the other hand there are others who possess great curiosity and they are

not so easily satisfied. One may be interested in the wood of the frame and consciously or unconsciously his mind will wander to questions concerning the chemical composition of the wood and what its behavior will be under different conditions of chemical treatment. It was such unsatisfied curiosity that caused one man to wonder how a silk worm could eat mulberry leaves, change the leaf fiber within its body by digestion, and then spin silk. He tried to produce the same change of fiber to silk in his laboratory and finally did make a filament which could be used for textiles. His early work was crude and was far from the present day production of beautiful "rayon" fabrics made from wood.

Another person looks at our picture. He appreciates its beauty but his curiosity, too, goes deeper. The effects are produced by pigments and he begins to wonder what they are. Some are made from natural minerals and others are synthetic. The reproduction of true colors is a difficult thing. Light, air, and age have their effects upon many colors. There are ever so many questions about these things. The oils mixed with the pigments have their part in the picture, too, and he wonders how the artist controlled the drying. If the observer is a chemist he may think of all these things in terms of experiments whereby truer colors and more lasting paints may result. If he is a manufacturer he may be inspired to seek more artistic color effects for his products or he may demand that more durable finishes be placed upon them.

Thus in considering one object, a painting, we may get the artist, the art lover, the scientist, the manufacturer, the advertiser and the salesman all looking at different angles of the same thing. We may ask the question then as to how we are going to classify things that interest men into the practical, the esthetic, and the theoretical. The fact that something has no use today does not mean that many uses may not be found for it tomorrow. It is almost certain that no uses will be found, however, unless someone is curious enough to learn all he can about that thing.

Chemistry has to do with all questions concerning the com-

position of material and with any changes in composition which substances may undergo. Thus iron ore is converted to iron; wood is converted into fabric for clothing; coal tar is converted in part to many brilliant dyes and in part to medicines; cornstarch is converted to table syrup or explosives; and limestone together with salt, water, and coal furnish the necessary raw material for the production of an artificial rubber. What such things are, how they are made up, and how they behave in the presence of other material and under various conditions such as heat or cold and weather is the very heart of the science of chemistry. The chemist, then, is a man or woman who is always insatiably curious about how substances are made and how they change.

Changing iron ore into iron requires a lot of energy in the form of heat, while the production of aluminum from its ore demands tremendous quantities of energy in the form of electrical power. The production of heat energy by the burning or combustion of fuels has been observed by everyone. The combustion of fuels within our bodies accounts for our bodily warmth as well as for the energy which we expend during our entire life. So long as this machine, which burns food for fuel, functions properly we are physically happy, but even small upsets in the chemical processes within our bodies may shoot our temperature up, give us a chill, cause considerable pain as in cramps or stomach-ache, stuff up our breathing with asthma, or may even kill us. Murder by poison is, of course, murder by chemistry. Thorough investigation has established the fact that all changes in composition which substances may undergo either produce energy in some form or require energy in order that they may take place. Thus chemistry is necessarily also interested in these energy changes which always accompany changes in composition.

There are some things already known that simplify somewhat the work of the chemist. In many instances these known things are summarized as laws. Just as the law of gravitation in physics expresses the behavior of a body with respect to the earth or to another body, so there are other statements

of fact which express chemical phenomena. These statements which have been devised through the years and which have to do with the changes in the composition of things are called chemical laws. A scientific law is not like a civil or criminal law. No legislature can pass it, no police are needed to enforce it; yet it always works and is never violated. Its formulation is a very slow process. Only after years of study, experiment, and checking the work of many investigators may the first attempt be made to express a chemical law. And there are many yet to be found and stated because even though they have not been investigated we are certain that there are rules of behavior, or laws, governing every chemical process.

Chemistry in a General Education. So much of what we

know or can learn about things falls within the scope of chemistry that it is not only worth a great deal but it is probably wholly necessary for every educated person to know something about this science. For those who plan to use its methods and the results as chemists, or chemical engineers, there is a long and rigorous period of training through which they must successfully pass and this must be followed by continual lifelong study which must never be slackened. But to the great majority of persons such training has no appeal because they are interested in and able to do other important jobs. However, these persons may easily develop an appreciation for the science of chemistry. To enjoy good literature one must read widely, know something of the background involved, and must spend considerable time with books but does not have to become a writer. In a like manner one may learn to appreciate music, history, philosophy, and all the other branches of achievement and knowledge which make for a rounded, full, and satisfying life. In every case a certain amount of exact study of one kind or another is required before a real appreciation is developed. So it is with chemistry. It is necessary to spend some time learning the methods by which science works in laboratories and factories as well as the processes of deduction, thinking and study which are at the foundation of chemistry in order that one may appreciate the practical applications that have produced most of the useful and beautiful

things we enjoy.

To some, the study of chemistry is sufficient reward within itself. But chemistry is really important because it touches many fields of men's activity. Some call it merely a service science because it contributes to greater achievement in the other sciences. It gives aid to astronomy, biology, geology, medicine, pharmacy, agriculture, economics, engineering, and to government. Whether one realizes it or not, chemistry is involved in almost everything seen, handled, or used during the day. In consequence every one of us knowingly or not has been building up a gradual knowledge of chemistry since early childhood. Of course, this knowledge may have been disorganized and entirely lacking in any relationships which give real meaning to the information. Therefore, for many, the inclusion of a survey of chemistry in their school or college course of study will tie this unorganized knowledge together, open up new fields of thought, and give new and thrilling meaning to life in general.

THE BACKGROUND OF CHEMISTRY

Records of the Past. In order really to appreciate the present position and importance of chemistry we should spend a little time looking back over the history of its development. The organized science of today is the result of countless years during which innumerable facts have been added to the common knowledge. Through the ages many men have sought for and found relationships between certain of these facts. The organized knowledge so resulting is known as the science of chemistry.

The written records to which we have access are in many cases obscure and one cannot always be sure of their meaning. However, we can be sure that written history covers but a very short space in the life of mankind. It becomes necessary, therefore, if we are to trace chemistry to somewhere near its beginning, to rely upon evidence in the form of materials used by men and dug from the remains of long-buried civilizations. We hope that the articles which they made in those early days reflected what they knew about things in general and it is upon this hope that we build our own ideas of their civilization. Even so, such a method can lead only to a meager conception of their life and ways of doing and thinking, and to an approximate date of their existence. Frequently such evidence as is dug from buried relics of buildings, from elaborate tombs or simple shallow graves or from ash heaps can be dated no closer than a thousand years to its real age. In many cases, however, rather exact estimates of age enable us to arrive at the culture of a certain period of time.

At the present time we are not interested in the politics or architecture of early man but we are interested in those things

which he used that have some connection with chemistry. Naturally, the articles usually found are of metal, pottery, glass, cement, pigments, and dyed cloth. The oldest findings are of gold but this does not help us in the search for the roots of chemical knowledge because this element occurs as the free metal in many parts of the world and many things may be shaped from it merely by pounding. It is evident that as early as 3000 B.C. man knew about copper, tin, lead, and iron which have to be dug as ore and subjected to chemical treatment before they can be used. Moreover, men this early had learned to make alloys by melting certain of these together. The use of bronze (a mixture of copper and tin) during this time has been fully established. No iron has been found which dates back further than 3000 B.C. but this does not mean this metal was not used at an earlier time. We presume that any iron older than 5000 years would have long ago returned to the oxide (rust) by the natural chemical process of rusting. The knowledge concerning iron was sufficiently advanced by 1300 B.C. to enable the Egyptians to make high-grade steel and this implies that men had had a very long experience with the metal. It seems clear that even in this early time some knowledge of smelting ores existed.

Early man's first practical chemical interests must have centered upon those substances known as the metals because they are strong, tough and lasting and may be shaped more or less easily for use. The word "metal" originally meant "the mines" and only later was used to indicate the product obtained from the mines. Early man related all things to his religion. Hence metals, being obtained from the interior of the earth which they conceived as a god, had an especially close relation to religion. They looked at the appearance of each metal and found it slightly different from that of the others. They observed that the behavior of each metal when it was heated, pounded, or pulled was peculiar to itself. Linking these observations with their religious beliefs they set up a sort of classification of the metals based upon their properties. Because seven was a number with religious or superstitious sig-

nificance the number of the metals was limited in the mind of early man to seven. So set were they on this belief that any new material found was classified not as a new metal but as one of these. One of their early lists of metals was further superstitiously identified with the sun and planets; Gold (for the sun), Silver (for the moon), Electrum, an alloy of gold and silver (for Jupiter), Iron (for Mars), Copper (for Venus), Tin (for Mercury), and Lead (for Saturn). Later the alloy electrum was dropped from the list and the pure element we call mercury was added. The order was shifted so that tin was assigned to Jupiter and this new element was assigned to Mercury. Strange as it may seem, this classification held for centuries and even though new metals were discovered they were classed as one of the above. The reason for doing this seemed to rest in the idea that the properties of the metals depended upon the relative amounts of earth, air, fire, and water which were associated in them. Even in the sixteenth century A.D. a worker in alchemy by the name of Paracelsus wrote, "There are many kinds of gold just as there are many kinds of apples or pears." The list of seven metals given above together with sulfur and carbon includes all the elements known at the beginning of the Christian era.

Articles of glass dating back to the earliest times indicate the use of this material in China, India, and Egypt. The story of the discovery of glass as told in early writings places its origin in the dry regions of Egypt where rock-like deposits of sodium carbonate served as an article of commerce. Ships loaded with this substance were supposed to have been wrecked along the sand coast and the sailors, it is thought, built fires behind low walls of these stones which served to shield the flames from the wind. The heat caused the sand and the sodium carbonate to melt together with the production of a type of glass which the sailors observed. The manufacture of much glass today employs sand, and sodium carbonate along with certain other material.

During the normal progress of primitive man he became acquainted with pottery, woven cloth, pigments, and certain

vegetable dyes. These things were probably accepted for what they appeared to be and no thought was given to their composition or to their chemical properties. Surely a considerable amount of knowledge was accumulated but each fact was sufficient unto itself with no relation to other facts. The writings which have been handed down from the time of Christ show that many rule-of-thumb recipes for alloys, glass, and other things were recorded but no organized science of chemistry existed even in infant form.

The Age of the Philosophers. There is definite evidence that the sixth century B.C. witnessed a wave of scholarly achievement throughout the civilized world. The roads of learning all seemed to come together in the country of Greece and it was there that the great philosophers developed. These men speculated much with their fine minds on the world and its meaning. Ideas concerning the nature of matter began to occupy them with the result that much of their writings dealt upon this subject. Probably the greatest thinker of the period was Aristotle (384-322 B.C.) who was also an indefatigable writer. In his writings one finds listed and systematically described all that he could learn of the knowledge accumulated by men until his time. Much of this may have been summarized from reports and writings of others and he seems to have had little interest in proving experimentally whether or not any portion of it was true.

From the point of view of chemistry we are interested in the contention of Aristotle that there are four primary elements: earth, air, fire, and water. These, he proposed, are formed by combinations of the four qualities: hot, cold, wet, and dry. In his mind fire was the combination of hot and dry while water was the combination of cold and wet. Because Aristotle failed to consider the possibility of water being hot and wet, as well as cold and wet, his statement remained unquestioned by other men for two thousand years. Such ideas and such a persistent belief in them may appear childish in the light of our modern experimental knowledge. In that time, however, even the great thinkers failed to recognize the fal-

lacy of their method of thinking. In the minds of these philosophers all knowledge could be gained by pure thought alone. Hence experiment was not only unnecessary but it was beneath their dignity. This mistake — the use of reason without experiment — held the progress of science at a standstill for two thousand years. As late as 1700 A.D. many men considered things true just because Aristotle had recorded them as such and no one thought it worth while to test their validity or, if one did, quite dared to make the test.

The Alchemists and the Origin of Chemistry. The center of knowledge shifted from Greece to Egypt about the third century B.C. and in the hands of the Egyptians a certain type of experiment thrived. No great philosophical thought prompted them, but curiosity and practical trade considerations did. Certain persons of the time thought poorer people would buy things made of cheap metal if they could be made to look like the costly ones. They set about to imitate the noble metals and soon cheap imitations found ready buyers among the poorer classes who were unable to possess the real articles of gold and silver. This business of making things to look like gold became a profession for some and probably served as a profitable source of income in many instances. Naturally, those who lived by this means clothed their work in the greatest of secrecy — like some manufacturers today who advertise "secret" processes and formulas — and permitted a veil of mystery to surround them. Somehow the name Chemeia, and later Alchemeia, became applied to this art without any known reason. Undoubtedly, Egypt was its birth-place and some think that the name Chemeia referred to the black soil of the Nile valley. It was then the art of the black country, or possibly, the black art, because it was so secretive. At any rate the control of the methods used, even though practical and experimental, still was linked with religion and rested with the priests so that only the initiated were permitted to learn their processes.

The old ideas of Aristotle prevailed. Many workers believed that the only differences between lead and gold lay in certain

properties which were common to the one and not to the other. They thought, therefore, that by removing some properties of lead and adding some properties of gold it was possible to convert lead into gold. Because of this idea there arose the group of alchemists who for fifteen centuries attempted what modern chemistry knows to be the futile task of transmuting the baser metals into the noble ones. Their constant experimentation driven by the lust for gold, entirely disorganized as it was, nevertheless brought to light many scientific facts. But whenever any of these were recorded secrecy was maintained and the language used was entirely void of any meaning to the usual reader.

By the sixth century A.D. another idea, that of the philosopher's stone, had crept into the thinking of those who studied nature. This was believed to be a most wonderful and powerful substance which acted as a yeast or a ferment and could of itself bring about the transmutation of lead or of mercury into gold. Gradually this mythical material began in the imagination of men to take on added powers and by the thirteenth century it possessed the ability to prolong life. Thus it also became known as the elixir of life. Naturally, all manner of means were tried to find it or produce it. Some even claimed to have found the secret but were careful never to give it away.

It is small wonder that by the fourteenth century the alchemists were under suspicion or branded as frauds. Like fake mining companies today or crooks who "borrow" money from easily influenced persons on the promise that they will share in a mythical estate, these fellows had lured prominent people to support them and buy them expensive materials on the promise that they were "just around the corner" from the discovery of how to make gold in abundance. The church, the populace, and the kings turned against them. They were forbidden by law to engage in their efforts. But every king kept a few of the sharper ones on his pay roll to serve him just in case anything ever came from their work.

The Development of the Scientific Method. An extraordinary interest in the physical universe began to develop rap-

idly about the thirteenth century. Roger Bacon (1214–1294), who was a progressive thinker of the time, first disputed the authority of Aristotle and expounded upon the unworthiness of pure thought. He insisted that one must learn the truths of nature first hand by doing experiments. It was three centuries later that a man known as Paracelsus, who was trained in medicine and in chemistry, contended that chemists should forget to look for the philosopher's stone and prepare medicine for the sick and that the medical profession should look to chemistry for help in medical practice. Paracelsus was not the kind of man one would like him to have been and his questionable behavior got him into no end of trouble but there is no doubt that he did start chemistry on the road toward being a useful science.

By the last of the seventeenth century this small beginning of scientific thought had grown considerably. The outstanding worker of this period was Robert Boyle (1627-1691), whose thoughts and efforts were probably the first ever to be employed primarily in the noble pursuit of investigating nature. He approached his work with a mind unbiased by previous writers and did not care what had been written by Aristotle. He preserved an attitude of real scientific skepticism toward all generally accepted theories. In his best known work, entitled The Spring of the Air, he described his experiments having to do with the effect of pressure upon an enclosed volume of air. In this planned study he proceeded in a manner contrary to the idea of the philosophers. He attempted to compile a large number of experimental facts. Then by a careful examination of these facts he was able finally to deduce the law which bears his name and which is a basic one in science. He discovered that the volume occupied by an enclosed quantity of a gas is inversely proportional to the pressure applied so long as the temperature does not change.

The first and second steps in what has come to be known as the *scientific method* were demonstrated by this work of Boyle. Generally this process involves four distinct steps. The first consists in the collection of a large number of experimen-

tal facts. In the second the experimenter formulates a general law in the light of the facts at hand. After many laws have been expressed, it is sometimes possible but difficult to take the third step and to propose a theory to account for the behavior described by the laws. The fourth, which attempts to establish the theories as truths, is the last and most difficult step.

The Beginning of Modern Chemistry. The work of Boyle opened the way for others and both stimulated and excited them. It led to a general consideration of the air, both physically and chemically. Then, as now, a new discovery of great importance drew other workers into the same field of investigation. With their varied interests and attitudes they were able to approach the study from different viewpoints and when gathered together as a whole their work was of great value. There were but few workers in those days and it took a long time to obtain results, but beginning with Boyle the advance of chemistry was as sure and as definite as was humanly possible.

Outstanding investigations followed those of Boyle. Men probed the nature and the cause of combustion, the rusting of iron and other metals, and human breathing. In their enthusiasm they evolved a theory which sought to explain all these things which had been observed. Because of the appearance of the flame during burning it was proposed that a fluid flowed out of the object being consumed by the fire and to this fluid they gave the name phlogiston. Later it was pointed out that all the products (gas, ashes, smoke, etc.) of combustion weighed more, when taken together, than did the original substance before it was burned. One would suppose that this would have destroyed the idea of phlogiston. But not so; it only changed the idea. It was then proposed that phlogiston was a fluid having a buoyant effect. Substances containing this fluid would then weigh less than they would after the phlogiston had flowed out during burning.

In the year 1774, Joseph Priestley, an English clergyman, discovered the gas which is now called oxygen but which he called "dephlogisticated" air. He explained that burning

took place in this gas so readily because it served as a reservoir into which the phlogiston from other substances could flow. Soon after the discovery of this gas, Lavoisier, a French scientist, saw the real relationship between air and burning and it was he who gave the world the modern conception of combustion. Since his time the progress of chemistry has proceeded with ever-increasing speed but even to this day many of the ideas of Lavoisier are accepted as truths and are upheld by scientific facts. It is no wonder then that Lavoisier is usually considered the "father of modern chemistry."

SUMMARY

The earliest records of chemical knowledge are those which have been dug from ancient ruins, tombs, and ash heaps whose age can be approximated only. Trinkets of gold which are found in the early remains tell us nothing of the chemical knowledge possessed by those people because gold was found as the free element and could be shaped by pounding. Vessels of tin, lead, and iron as well as those of brass which have been found indicate an advanced experience in metal working since these metals were obtained from their ores through chemical processes.

The earth was closely connected with the religion of ancient times and all of the metals taken from the earth were accorded religious significance. The number seven was strangely worshipped and only seven metals were believed to exist. These seven were named for the sun, moon, and planets as follows: gold for the sun; silver for the moon; tin for Jupiter; mercury for Mercury; iron for Mars; copper for Venus; and lead for Saturn. Each of these metals was thought to possess its properties because of the relative amounts of earth, air, fire, and water which it contained. Only two other elements, sulfur and carbon, were known at the time of Christ. Though many rule-of-thumb recipes for alloys, glass, and medicines existed there was no organized chemical knowledge.

During the fifth and fourth centuries B.C. the Greek phi-

losophers speculated concerning the nature of the universe. Aristotle was the outstanding one of these and he is best remembered. He believed that pure thought alone was enough to solve the questions of the time and looked down upon experiment as undignified. His ideas prevailed for two thousand years after him.

Chemical knowledge became available to the Egyptians during the third century B.C. and with them experiment thrived. It was in Egypt that the term alchemist originated and it is supposed to have reference to the black soil of that country. Those who practised the art were quite secretive and control of it was in the hands of the priests.

During the sixth century A.D. the idea of a philosopher's stone came into being. This was a substance which was thought capable of turning the base metals into gold. By the thirteenth century this same fantastic material was believed to have the power of giving everlasting life and was called the elixir of life. The frauds resulting from such ideas as these brought the alchemists into disrepute and the practice of their art was outlawed.

The first scientific thinker was Roger Bacon who lived in the thirteenth century. He outlined the ideals of the scientific method. Three centuries later Paracelsus caused the physicians to turn to chemistry for help and started the chemists on the road toward usefullness. The beginning of chemical science is traced directly to Robert Boyle who in the seventeenth century planned and carried out researches according to the scientific method. His best known work had to do with the effect of pressure on an enclosed volume of air.

Soon after Boyle a great amount of investigation was done. The idea of phlogiston was presented to explain combustion. The discovery of oxygen by Priestley gave the final blow to the phlogiston theory due to the brilliant ideas of Lavoisier.

REVIEW QUESTIONS

1. What facts do you know which would indicate a long life for articles of gold but a shorter one for articles of iron?

2. What reasons can you give to account for the long lasting

qualities of glass?

3. What great error was made by the Greek philosophers?

4. For what reasons did the alchemists thrive?

5. Do you know of any reasons why a person might get the idea today that there are many kinds of gold?

6. List the four steps in the scientific method.

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THE ATMOSPHERE: PHYSICAL PROPERTIES

The Law of Boyle. The most common thing in human experience served as the starting point for the research which Boyle undertook. Because of its close relationship to our lives we shall consider his work on the properties of the air and shall also consider the component parts of which the air is a mixture.

That the air has weight was shown by Galileo as early as 1600 A.D. and thus it was considered as being made up of matter such as other things were. It was conceived as being a most peculiar type of matter, however, since it could fill a lot of space, or if properly treated it could be compressed to occupy only a little space. Some thinkers proposed that the air might be a material in the form of an indefinite coiled spring which could adjust itself to fit any shape of space. In other words, it was thought to be everywhere and continuous, except that no difficulty was encountered if one desired to enclose only a certain small amount of it. Other students of air, however, noted this fact and, from it and other observations, considered air as discontinuous like iron, or water.

Regardless of whatever form air might ultimately take Boyle desired to know more of what it was like and how it behaved, in other words its physical properties. He enclosed a suitable volume of the gas (air is a gas) in a tube and by means of a plunger (mercury) he was able to change the applied pressure and to set down accurately the volume of air in the tube that he noted with each pressure change. He found that as he stepped up the pressure the volume of air became smaller, and that as he lowered the pressure the volume increased. Now

Boyle was interested to see if there was an exact relationship between the pressure change and the volume change so he made use of a piece of apparatus which was designed to gauge these very things. By pouring mercury into the open end of

a U tube such as shown in the diagram he was able to increase the pressure upon the air enclosed in the other arm. By measuring the height of the mercury in each arm of the tube he could calculate both the applied pressure and the resulting volume of air. Much to his satisfaction, he found that by doubling the pressure the volume of the gas was reduced one half. For other pressures he obtained exactly corresponding changes in the volume. His entire experimental work in this field may be summed up by the statement which is called Boyle's Law. This law states that if the temperature of an enclosed volume of gas is kept constant the volume which it occupies is inversely proportional to the pressure which confines it. For those who like to express knowledge con-



Fig. 2. Apparatus Used by Boyle

cisely for easy handling and who do work with gases this law is expressed in a simple mathematical statement as follows:

pv = c

By this is meant that the pressure, expressed in suitable units, multiplied by the volume, also expressed in appropriate units, is equal to a number which is constant for a given amount of gas. Thus to retain this relationship the volume must decrease if the pressure is increased. This principle seems quite simple now that the work has been done and you and I can sit in our classrooms or study and say, "Of course, how could it be otherwise?"; yet this bit of knowledge so expressed was built up over years, by great effort, and still is of profound importance.

The Barometer. The common method of measuring the pressure of a gas was developed just before Boyle began his work and without it he would have been seriously hampered.

Down through the ages of scientific discovery, progress has always waited upon the production of new implements and tools with which to work. Sometimes these have been simple practical things built out of wire, rubber, cork and glass, sometimes elaborate machines. In this case the tool was a simple tube filled with mercury and inverted in a dish of mercury. Torricelli, a student of Galileo, set up such a piece of apparatus

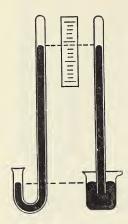


Fig. 3. Two Forms of the Barometer

and found that the mercury within the tube remained at a higher level than that outside of the tube. This column of mercury, he explained, was held up by the weight of the volume of air exactly the size of the tube and extending up to the sky pressing on the mercury in the dish. Since this served to measure the pressure of the air it came to be known as a barometer (Greek baros = weight + meter = measure) and is still used for this purpose. By measuring the height of the column of mercury above the level in the dish one is able to arrive at an actual value for the air pressure. Since the pressure is proportional to the height of

the column of mercury it is customary to express the pressure in terms of this distance. Thus a barometric pressure of thirty inches means that the mercury column in a barometer stands thirty inches above the level of the mercury in the outside dish. For scientific purposes (because the 10 unit metric scale is easier to use than the English units) this distance is measured in centimeters rather than in inches.

The Thermometer. It was noted by Galileo that air expanded when it became warm and the first thermometer was built by him, taking advantage of this fact. The modern thermometer has been developed from this early observation. We are accustomed to expressing the intensity of heat by means of units called degrees but many people do not stop to consider that these degrees, or units, are defined and set by men and are not God-given. As is usually the case when men devise a

definition, there has been some divergence of opinion as to the exact change in heat intensity which we shall call one degree. Of course, it really does not matter what unit we use except that it becomes more understandable when every one means the same thing by the term.

Temperature Scales. In order that a better understanding may exist it is customary for scientists to define their terms

by means of things which occur in nature and which you or I may easily observe. For the graduation, or marking, of thermometers there are two conditions of temperature which may be easily produced and which are constant. One of these is the temperature of freezing water, or of melting ice, and the other is the temperature of boiling water under a specific (fixed) atmospheric pressure. With these two points on the scale of temperature, it is an easy matter to divide the distance between them into any number of equal parts. In 1714 G. D. Fahrenheit, a physicist of Danzig, chose to make 180 divisions between these two points and such a scale bears his name. By marking off degree distances of the same length above and below these two points other temperatures may be indicated. In order to arrive at a zero point, Fahrenheit mixed ice

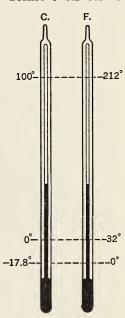


Fig. 4. Comparison of Temperature Scales

with salt and considered the resulting temperature the coldest obtainable. This new temperature was thirty-two divisions below the freezing point of water and on this basis he gave values to each of his points. Some time later another worker, Celsius, a Swedish astronomer, proposed the centigrade scale of temperatures which has been adopted for all scientific work because it is more simple and convenient. He chose the same two reference points but to the temperature at which water freezes he assigned 0° and to the temperature at which water boils he

assigned 100°. These two scales of temperature are compared

in the accompanying figure.

Variation of the Volume with Temperature. It has already been noted that Galileo discovered how the volume of air increased as it was heated, shrank as it was cooled. But without any means of measuring the temperature changes, it was impossible for him to make a study of this change in volume. After the temperature scale was fixed this study was made by a French physicist, Charles, and later by another Frenchman, Gay-Lussac. When their data were completely assembled it was observed that a quantity of any gas including air changes in volume by a definite amount for each degree change in temperature. If a definite quantity of air, or any other gas, was measured at 0° centigrade and then cooled one degree they found that the volume always decreased by 1/273 of the original volume. By cooling still further the gas was observed to decrease 1/273 of its volume at 0° for each and every degree it was cooled. This process was found to be entirely and exactly reversible and an elevation of the temperature produced a corresponding increase in the volume.

Absolute Zero. The described facts which deal with the change of volume with temperature have brought forth a new scale of temperatures. One can easily imagine a quantity of gas being cooled more and more until it has reached a temperature 273° colder than 0° C. By further use of the imagination one can describe what has happened to the volume of the gas during this cooling. If each degree the gas is cooled decreases the volume by 1/273 of the volume at 0° C. then surely at -273° C. the volume would be zero. However, if we try it, something goes wrong and we never would get our gas to shrink to nothing even if we could force the temperature down to -273°. No gas can be cooled to such an extent without first becoming a liquid and then the volume changes do not follow the described course. It is possible, though, for us to choose this point which is -273° C. and use it as the theoretical starting temperature. It is thus called the absolute zero and is defined as the temperature at which a gas, if it did exist, theoretically would possess no volume if it continued to decrease in volume at the rate of 1/273 of its volume at 0° C. for each decrease in temperature of 1° C.

The only difference between the centigrade and absolute scales of temperature lies in the designation of the zero point. By adding 273 to the centigrade reading one obtains the absolute temperature. For most purposes the temperature expressed in absolute degrees has no significance other than is shown by the centigrade reading but for all scientific chemical work dealing with gases and for certain other scientific purposes the absolute scale must be used.

Charles' Law. After thus defining a scale of temperature which is used in working with gases it is possible to express the data of Charles and of Gay-Lussac in an understandable manner. This is all summed up in a law which is called Charles' Law or Gay-Lussac's Law and it is stated as follows: If the pressure upon a gas does not change, the volume of the gas varies directly with the absolute temperature.

In order that this law may be easily used it is expressed mathematically by the simple proportion,

$V_1:V_2::T_1:T_2.$

This may also be expressed in words at much greater length and more awkwardly for the specialists by saying that when a gas is heated the volume before heating is to the volume after heating as the absolute temperature before heating is to the absolute temperature after heating. An example will make this more clear. Suppose that a volume of air measuring 100 cubic centimeters at 0° C. is heated to 273° C. and we wish to calculate the volume it should have according to Charles' law. Expressed in absolute degrees the first temperature becomes 273° and the second temperature becomes 546°, or twice as much as the first. Since the absolute temperature has been doubled we must expect the volume of the gas to double also and the new volume is calculated to be 200 cubic centimeters. The volume change accompanying any other temperature

changes may be calculated by the use of the mathematical expression given above.

A statement similar to Charles' law can be made with respect to pressure changes which accompany temperature changes. If the volume of a gas does not change, the pressure on the gas varies directly with the absolute temperature.

Standard Conditions. From the previous discussion it becomes plain that the volume of an enclosed amount of air, or other gas, depends upon the applied pressure and upon the absolute temperature which prevails at the time. This may also be expressed by saying that the pressure of an enclosed quantity of air, or other gas, depends upon the volume of the enclosure and upon the absolute temperature. Since the chemist frequently deals with gases it is necessary that he set up a certain standard reference pressure and temperature. For convenience, the pressure so chosen represents the average atmospheric pressure at sea level which is equal to that of a column of mercury 760 centimeters high, and the temperature chosen is that of melting ice which is 0° C. or 273° Absolute. These are called standard pressure and standard temperature and are referred to collectively as standard conditions. With them the chemist knows what he is doing when he handles a gas and his results may be compared with those of others.

A Mental Picture of a Gas. It has been said that the early investigators, previously discussed, were interested in nature and had a desire to explain natural phenomena. After the facts were collected by experiment and the laws were stated in the light of the facts, men began to formulate theories as to the make up of the air and of gases in general. It was early shown that all gases behave alike toward changes in pressure and in temperature so it was natural to conclude that they are all alike in some respects. By a consideration of the known facts concerning gases it is possible to construct a mental picture of their physical structure.

Since it is possible to compress a gas to a very small fraction of its original volume one must conclude that it is not like a hard compact substance. Instead there is much free space

within the gas which is not occupied by rigid matter. If you could see it, it would be more like a sponge than a piece of stone. Another indication of this porous nature of gases is given by the property known as diffusion. If a bottle of strong perfume or other material with a strong odor is opened in a room it takes but a little while for its odor to penetrate to every corner. The odor is carried in a gas and the fact that it passes through a space which is already "filled" with another gas (air) shows that the air must enclose quite a bit of free space.

The source and direction of the pressure which a gas exerts presents a question of considerable importance. It can be easily demonstrated that the pressure of a gas is exerted equally in all directions if we neglect the very small difference due to weight. With a height of gas such as that of the atmosphere this difference of pressure due to weight can be easily detected, but for measurable quantities of a gas the effect of gravity is too small to notice. A pinhole opening may be made in any part of the top, bottom, or sides of a container which confines a gas and immediately the gas will begin to move out of the container and away. Thus the direction of the pressure is not fixed. The fact that the gas *moves* out of the opening and *moves* through another gas gives reason to the idea that possibly a movement exists in a gas all of the time. If there is a motion of something within a gas then the explanation of gas pressure becomes simple. Whatever it is which moves, it must surely have weight. And when an object which has weight is moving it batters or presses at anything which makes an effort to stop it. A hammer may be used to drive a nail into a piece of wood. This is done by moving the hammer (a weight) at a high speed so that it strikes the head of the nail. The faster the hammer moves the greater the force which it exerts upon the nail which stops it. The pressure so developed drives the nail into the wood.

If we imagine a gas as being made up of innumerable small weights which move at random in all directions, then we will expect them to exert a pressure upon the walls of the thing

in which they are contained. The amount of this pressure will depend upon the number of these moving weights and the speed with which they strike the wall. Since the particles are imagined as moving in all directions we expect the resulting pressure to be exerted in equal amounts in all directions. These moving particles which thus are imagined as having both weight and motion are called *molecules*.

It has already been pointed out that an increase of temperature produces an increase in the pressure which a gas exerts. Now if we have small particles in motion the only way to vary the pressure which they exert is to vary the speed with which they move since their weight or mass is not changeable. We may conclude from this that a rise in temperature increases the speed of the moving molecules.

Molecules of different gases in a mixture do not settle out in layers but remain more or less permanently mixed. If a gas of very low density (this means that the molecules are very light) is mixed with a gas of very high density (the molecules are very heavy), some separation will naturally result due to the slower motion of the heavier gas. This separation cannot be observed except in a very long vertical column of the mixture. It has practical applications however. War gases mix somewhat with the air, but being heavier they settle to the ground and linger there. In the case of the air such a column exists, and it is found that some separation takes place. Near the surface of the earth the carbon dioxide content of the air is quite small (0.035 percent) but at higher levels this concentration becomes less and less until it finally reaches zero at high altitudes. On the other hand there is little or no hydrogen to be found near the earth but at high altitudes this gas, which is the lightest known substance, appears in ever-increasing amounts. The very outer portion of the atmosphere is probably composed of pure hydrogen but, of course, it is extremely rarefied. That is, it is under very little pressure and is very much expanded. Changes in the composition of the air do not take place suddenly, as we go upward, as if layers existed, but slowly over miles of change in elevation.

A gas does not settle to the bottom of a closed container even if the container is left undisturbed for years. This is contrary to human experience with things large enough to be seen and handled. The best rubber balls dropped on a hard floor will soon cease to bounce; but they do not have to be of such material as rubber in order to bounce, since steel balls dropped upon a hard smooth surface rebound remarkably well. This

property of bouncing away from the object which is struck is a result of the elasticity of the bodies. The more elastic objects are the greater the amount of their energy of motion they retain after striking each other. So long as the temperature of a container of gas remains fixed the molecules appear to lose none of their energy of motion (kinetic energy) so we feel

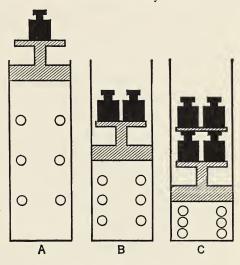


Fig. 5. Boyle's Law

justified in assuming that the *molecules of a gas are perfectly elastic*. This does not mean that the molecules are never slowed down or caused to move more rapidly but it does mean that if one molecule is slowed down the kinetic energy is transferred to another, which, as a result, moves more rapidly. In this fashion the average energy of all the molecules remains the same.

The explanation of Boyle's law according to these ideas is fairly simple. Suppose that a cylinder containing a number of gas molecules is fitted with a tight, movable piston as illustrated in the figure. In the first case (A) the pressure of the molecules in motion is just sufficient to hold up the weight resting upon the piston. If now the total force on the piston is doubled (B) the volume occupied by the gas becomes just half

of the original volume and as a result the number of molecules contained in this volume is twice the original number. Since the speed of the molecules has not decreased, it must be true that the total pressure against the piston has doubled. Thus our mental picture exactly fits the facts as given by Boyle's law.

The Kinetic Theory of Gases. The mental picture of gases which has been presented is termed the *Kinetic Theory of Gases* and it may be summarized in a few brief statements.

1. Gases are composed of minute particles called molecules, which are in motion in a perfectly random fashion.

2. The average kinetic energy of these molecules is proportional to the absolute temperature.

3. The pressure exerted by a gas is proportional to the number of molecules confined in a unit of space.

4. Molecules of a gas are perfectly elastic, losing none of their kinetic energy upon impact with other molecules at the same temperature.

5. Except at very high pressures, the volume of the molecules themselves is very small in comparison with the space between the molecules.

Importance of a Theory. The formulation of the kinetic theory of gases illustrates the third step in the scientific method. An idea of the structure of a gas has been expressed which appears to fit the laws which are based upon experimental facts. Thus while the actual visible proof of the proposed theory may never be accomplished, yet in the meantime the accepted hypothesis serves as a valuable aid in the task of understanding nature. Even though it may be false it surely is far better than no theory at all. As a matter of fact this kinetic theory is becoming more and more fixed as a truth as each bit of evidence is presented. It has been and may again be necessary to revise points here and there in the theory as time goes on, but in every case the revisions bring about a more complete and accurate scientific statement; one which more nearly fits all the facts. Whenever the known facts do not appear to fit the theory, scientists make these misfits the immediate cause for investigation. Always in such cases the facts are gone over

again and redetermined in such fashion as to eliminate all possible sources of error and then if they still do not fit the theory there is nothing to do but change the theory. In this manner the theory is shaped and reshaped until it approaches, though may never reach, an actual statement of the truth about nature.

Deviations from the Gas Laws. The laws which describe the behavior of gases do not in any way apply to liquids or to solids. All substances which exist as gases may also be converted to liquids or to solids, if the temperature is low enough and the pressure is high enough. Liquid air and solid carbon dioxide are now common things. It seems that the change from a gas to a liquid takes place because the molecules are close enough together to attract each other and are moving so slowly they cannot get far apart.

According to the kinetic theory of gases the molecules are very far apart so that the space not occupied by them is far greater than the space actually occupied by the individual molecules. Under such conditions the forces of attraction between the molecules become infinitely small and the gas laws describe the behavior of gases almost exactly. If, however, the pressure applied is great enough to force the molecules quite near each other the natural forces of attraction become large and the molecules are drawn still more closely together and may become liquid. Under such conditions of high pressure the law of Boyle cannot hold and it is common experience that such is the case.

Critical Temperature. So long as the speed of the molecules is great enough to prevent their cohesion to form a liquid, a gas cannot be changed to a liquid. As a matter of fact, when the temperature of a gas falls low enough so that the speed of the molecules is insufficient to overcome the forces of attraction between the molecules, the gas condenses to a liquid. The attraction between the molecules of some gases is much less than for others. Because of this, some gases must be cooled much more than others before they will become a liquid. The temperature to which a gas must be cooled before any amount

of pressure will cause it to liquefy is called its critical temperature.

In the case of certain gases even large pressures are insufficient to bring about their liquefaction at ordinary low temperatures. Such temperatures are evidently above the critical temperatures of these gases. In these instances additional pressure does not produce the decrease in volume which Boyle's

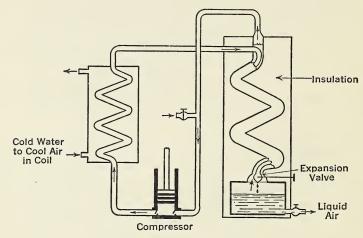


Fig. 6. Liquid Air Machine

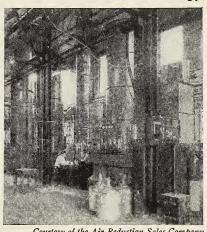
law requires. There is reason to believe that the molecules have been forced together and that the free space between them is quite small compared with the volume of the molecules themselves. It seems, too, that the individual molecules are not compressible and thus additional pressure fails to bring about a further decrease in volume.

These deviations in the general behavior of gases do not affect the kinetic theory but on the other hand the kinetic theory makes possible the explanation of these experimental facts. The gas laws apply only to gases having no attraction between the molecules, thus having no cohesion, and having molecules which occupy none of the volume of the gas. Naturally no such gas exists and therefore we speak of *ideal* or *perfect gases* as meeting the requirements of the gas laws. Under ordinary conditions of temperature and pressure the deviations from ideal

behavior are so slight that no corrections need be made and we may consider the gas laws as expressing exactly the behavior of gases.

Heat of Condensation. From the foregoing discussion it becomes apparent that both pressure and cooling are necessary to convert gases into liquids. For some gases the amount of cooling necessary is obtained at ordinary temperatures while for others, such as air, the temperature must be carried quite low. High pressure alone or low temperature alone does not bring about the liquefaction of air. When the kinetic energy

of the molecules can no longer overcome the attraction between the molecules there is a sudden loss of considerable motion and the molecules cohere. This sudden coming together of the molecules releases energy and it is given up in the form of heat. The temperature of the gas-liquid mixture does not change because of this evolution of heat since it merely represents the energy required to keep the molecules apart at the tem-



Courtesy of the Air Reduction Sales Company

Fig. 7. Columns and Equipment for the Liquefaction of Air

perature of the process. For some gases this energy loss is quite high but for others it is rather small. Naturally this heat produced is called the heat of condensation.

The ordinary condensation of steam offers a suitable example for consideration. When steam strikes a cool object and condenses, its heat of condensation is liberated. This amounts to a considerable quantity of heat and accounts for the seriousness of steam burns.

Liquefaction of Air. In the actual operation of a plant which produces liquid air it is necessary to take advantage of the facts mentioned. An air pump compresses the air and the heat evolved is taken away by water or by the outside air. By permitting a part of the compressed air to expand and therefore cool in an insulated container heat is taken from the remainder of the compressed air rather than from the surrounding atmosphere. Thus a part of the compressed air is made much colder. By repeating this or similar processes a part of the air is cooled enough to liquefy. It is by this means that thousands of tons of liquid air are produced annually. The diagram shows the essential parts of a liquid air machine. The compressed and cooled air enters the liquefier through the small inner tube and

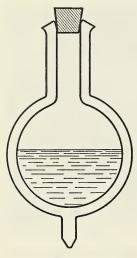


Fig. 8. Dewar Flask

it expands through the jet at the end. The expanded gas returns to the pump by the outer tube and helps to produce additional cooling. In this manner the air which escapes through the jet is reduced gradually to a very low temperature until at last it is cool enough to become a liquid.

The Thermos Bottle. It has been said that the evaporation of a liquid requires considerable heat and this is also true for liquid air. By permitting liquid air to evaporate it is possible to produce temperatures as low as —190° in laboratory apparatus and then to cool chemicals for experiment. Because the rapid

addition of heat to this liquid produces boiling which is more like an explosion it is necessary to store liquid air in insulated vessels. One of the most satisfactory of these is the *Dewar flask* which is really a flask within a flask with the space between the walls evacuated. You know this as the ordinary thermos bottle. To prevent heat changes due to radiation the walls are usually silvered. In such a container liquid air may be kept for several days.

SUMMARY

The *barometer* was invented by Torricelli in order to measure the pressure of the atmosphere.

The thermometer was developed from a simple device made

by Galileo.

The Fahrenheit scale of temperature uses the temperature of freezing water as 32° and that of water boiling at sea level as 212°.

The *Centigrade scale* of temperature was proposed by Celsius and uses the temperature of freezing water as 0° and that of boiling water at sea level as 100°.

The Absolute scale of temperature is obtained by adding 273 to the centigrade temperature. This scale has to do with the behavior of gases.

Boyle's Law states that if the temperature is kept constant the volume of an enclosed quantity of gas changes inversely with the pressure applied.

Charles' Law states that if the pressure on an enclosed quantity of gas is kept constant its volume changes directly as the absolute temperature.

Standard conditions are taken as a temperature of 0° C. and

a pressure of 760 mm. of mercury.

The Kinetic Theory has been devised to give us a mental picture of a gas. It proposes that a gas is made up of small particles called molecules which are relatively far apart and in violent motion. The velocities with which these particles move depend upon the temperature only. If gases are cooled so that their molecules move less rapidly or if they are put under pressure so that their molecules must remain close together the laws of Charles and Boyle fail to describe their behavior correctly.

The *critical temperature* of a gas is the temperature above which the molecules possess too much energy to permit their adhering to each other as in the liquid state, regardless of the applied pressure. Below the critical temperature a gas may be caused to liquefy by increasing the pressure alone.

The heat of condensation is the energy released by the molecules of a gas when they are condensed to the liquid state. It represents the energy which holds the molecules of gas apart. Conversely, the change of a liquid to a gas or the expansion of a compressed gas absorbs energy in the form of heat and low temperatures may be produced by the use of this fact.

The Dewar flask, or thermos bottle, serves for the storage of some liquefied gases because its construction prevents the

absorption of great quantities of heat by the liquid.

REVIEW QUESTIONS

1. Explain what happens as you fill a small rubber balloon with air from your lungs.

2. If the opening in the filled balloon is securely closed and it is placed in a heated room what will happen? Why? Use the kinetic

theory in the explanation.

3. Suppose you have two tanks having a volume of one cubic foot each. One tank is filled with oxygen at a pressure of 300 mm. of mercury and the other is filled with carbon dioxide at a pressure of 400 mm. of mercury. Now by means of a pump transfer all of the oxygen into the tank with the carbon dioxide. What will be the total pressure in this tank of mixed gases if the temperature is kept constant?

4. How is it possible for an inflated automobile tire to hold up

such heavy loads without being flat on the bottom side?

5. Give some reasons for the assumption that the molecules of a gas are far apart and the molecules of a liquid are close together.

6. Give some evidence for the statement that the molecules of

a liquid tend to stick together.

7. What would happen if a slow moving molecule were to hit a fast moving molecule "head on"? How does this differ from your experience with other things?

8. Would the height of water in a barometer containing water be any different from the height of mercury in a barometer filled

with mercury? Why? How much?

9. Starting with 100 cubic centimeters of air at 0° C. and 700 mm. pressure, calculate the volume it would have if the temperature remains the same and the pressure is increased to 1050 mm.

With the pressure remaining at 1050 mm. to what temperature must the gas be heated in order to give the original volume of 1000 cubic centimeters?

10. A temperature of 1° C. would be what temperature F.? 50° F. is what C.°?

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THE ATMOSPHERE: ITS COMPONENTS

Air is a Mixture. In the commercial production of liquid air it is customary to remove the dust particles, water vapor, and carbon dioxide before the final step of liquefaction. The last two of these are converted to liquids long before the remainder of the air liquefies and thus they may be separated quite easily. If liquid air is permitted to evaporate, the different substances which are contained in it boil off at different temperatures. About four fifths of the liquid boils off at —195.8° C. and the resulting gas is quite inactive chemically. It is nitrogen. The remaining one fifth of the liquid air is almost pure oxygen and will not boil at this low temperature. If, however, the temperature is permitted to rise to —183° C. boiling again takes place and oxygen gas is formed.

It is an established fact that pure liquid substances have definite boiling points while most mixtures of pure liquids may be separated, at least in part, by the boiling process. Since liquid air may thus be separated into at least two different substances with different boiling points we can assume that liquid

air itself is a mixture rather than a pure liquid.

There are some persons who require still other evidence that air is a mixture and for them there is another striking example. Whenever a pure substance such as salt or sugar dissolves in water it does so as a whole. The salt which is in solution has exactly the same composition as the salt before being put into solution. This is not true in the case of air. If freshly boiled water, which contains no air, is cooled and stirred in the presence of air we find that some air is dissolved in the water. Now by boiling the water again we can collect the dissolved air

which is expelled by this process. The air so collected is much richer in oxygen than ordinary air. If the oxygen and nitrogen were chemically combined this would not be true.

OXYGEN

It has already been mentioned that respiration and burning furnished a considerable field of thought for the early chemists and other scientifically inclined workers. Just before 1700, John Mayow proposed that air contains a gas which promotes these processes. This gas unites with metals when they are burned, according to his viewpoint, and it changes the blood from the venous to the arterial form. The theory of phlogiston was proposed during the same year by Becher and for three quarters of a century it overshadowed the work of Mayow. According to this theory all combustible substances contain "phlogiston" which is set free when they burn. The flame which could be observed easily was produced by the outward flow of this substance into the air. Since combustible materials would not burn in the absence of air it was quite obvious that air took up or absorbed this phlogiston.

In 1774 Priestley was interested in heating all of the substances he could find. For this purpose he used a large lens by means of which he focused the rays of the sun as a source of heat. By enclosing the substance to be heated over mercury in a barometer-like tube he was able to collect any gas which was evolved during the heating. It was during these experiments that he happened to heat the oxide of mercury and from it he got a gas which caused a candle to burn with extreme brilliance. He had actually prepared pure oxygen but he failed to recognize his discovery and called the gas "dephlogisticated air." At the time of his death in 1804 he believed that the theory of phlogiston had been established.

In 1777 a publication appeared which showed that a Swedish worker by the name of Scheele had actually prepared oxygen two years before Priestley did. He had heated a number of substances which liberated this gas. The evidence shows clearly

that he was on the verge of realizing the importance of this discovery though he never succeeded.

Soon after Priestley made known his work on mercuric oxide, Lavoisier took up the experiments. He was already interested in combustion and had shown that tin actually takes something from the air when it burns. He repeated the work of Priestley at once. Then in order to get better proof he formed his own oxide of mercury by heating pure mercury in the presence of a measured volume of air. After many days of slow heating he observed that the volume of the air had shrunk by one fifth of its original amount and there was a thin coating of red powder over the surface of the mercury. The gas left over the mercury was not like ordinary air in that it would neither support a flame nor sustain life. When he carefully removed the red powder and heated it strongly it gave a volume of gas exactly equal to the volume of the gas which disappeared when the powder was made. The liberated gas had the properties of air but it was much more active. Thus he was able to show that air is a mixture of two things; one of them active and the other inactive. He proved conclusively that combustion is due to the union of this active substance with the material burned.

By some means Lavoisier got the idea that this active gas was essential to the formation of all acids and he named it oxygen (acid producer). This idea was entirely wrong but the name has remained.

This element, oxygen, makes up approximately half of the total weight of the earth's crust which includes the air, water, stones, clay, and other material in that part of the earth which we know. A substance which occurs in such abundance must also, of course, be of considerable importance but because of the nature of oxygen its importance is far greater than even its relative abundance would indicate.

Burning of Fuels. Our greatest supply of energy comes from the union of ordinary fuel with the oxygen of the air. This energy is released in like amount regardless of whether this union takes place in the firebox of a furnace, in the cylinder

of an engine, or in our own bodies. The fuel and the oxygen taken separately contain much more energy than do the substances which are formed by their union (carbon dioxide and water). The excess energy is released in the form of heat and light. The products of the combustion have compositions which are different from oxygen alone or fuel alone, and also they have characteristics (properties) which likewise differ from those of the separate substances.

Rusting. Iron and some other metals, when exposed to the air, slowly combine with the atmospheric oxygen and "burn" by the process which we call rusting. This destruction goes on in an uninterrupted manner unless the iron is galvanized, painted, or treated in other ways to prevent it. Because proper steps are not always taken to prevent this slow burning process we find that steel bridges become unsafe, railway rails become thinner, and automobile bodies, farm tools and other implements begin to fall apart. The toll taken by rust cannot be calculated with any degree of certainty, but we are sure that it is enormous. As a rule this process requires moisture and carbon dioxide as well as oxygen, but the metal is consumed just as though it were burned in a fire as a fuel. The total heat evolved is quite large but it radiates into the air and it is liberated too slowly to raise appreciably the temperature of the metal. Here again we find that the energy stored up in the iron and the oxygen taken separately is greater than the energy stored in the iron oxide which is formed by their union. The iron oxide does not look like iron and it has none of the other properties of iron.

Decay. We are all accustomed to the removal of leaves, dead wood, refuse matter, and other undesirable material by the process of decay. All too often many useful things likewise are consumed by this same method. Frequently the change is speeded up by the action of bacteria but in all cases the essential change is due to the union of the substances present with the oxygen of the air. Heat is liberated in this case, too. Many times we see evidence of this. A pile of grass which has been slightly moistened will become quite hot. Layers of

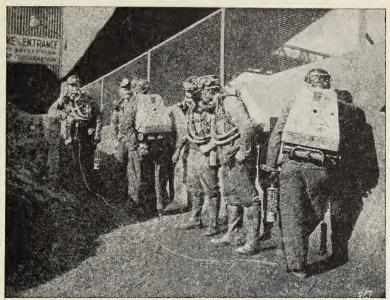
straw and manure from stables are frequently used to supply

heat to young plants during the early spring months.

This decay of organic matter appears to liberate more heat than does the rusting of iron but this is not necessarily so. The union with oxygen takes place more rapidly and the outer layers of material serve as effective insulation so that the heat liberated cannot get away so quickly.

Spontaneous Combustion. All of us have noticed that things which burn at all will burn much more rapidly if they are hot. Since the amount of heat liberated within a certain time depends upon the rapidity of the burning it naturally follows that the faster a thing burns the hotter it will get. When a quantity of combustible material begins to unite with oxygen its temperature tends to rise and if the heat produced cannot get away, the temperature does rise and the rate of union with oxygen increases. This produces still higher temperatures within the mass of material and a still greater rate of oxidation occurs. After a time a temperature is reached when the additional union with oxygen will produce a flame. When this occurs it is called spontaneous combustion. Cases of fire from this cause are common and must be guarded against even in the home. Pieces of cloth saturated with certain types of oil used in cleaning furniture, cloth or waste soaked in paint or varnish, and old newspapers neatly stacked in the basement or attic are all possible sources of such fires. Other cases of spontaneous combustion have been noted frequently in flour mills and grain elevators. Here the air may become filled with a fine dust which is extremely active toward oxygen and the presence of an electric spark or hot bearing is sufficient to touch off the entire atmosphere and results in what is known as a "dust explosion."

In all cases of spontaneous combustion there are certain conditions which are present. The material concerned is one which presents a large surface so that great amounts of oxygen can get at it. The reaction with oxygen must proceed rapidly enough to produce an appreciable amount of heat and this heat must be kept in for a while by surrounding insulation so



Courtesy of the Mine Safety Appliances Company

Fig. 9. Two-Hour Breathing Apparatus for Mine-Rescue Work

that the *kindling* temperature is reached. For instance, a cloth soaked in paint will be entirely harmless if it is spread out so that cool air may get to it freely.

Respiration. The respiration of every thing which breathes also involves the direct union of oxygen with other material. A part of the oxygen which enters the lungs combines with the red corpuscles of the blood and is carried to all parts of the body where a slow "burning" takes place. The fuel for this burning process is furnished by the food which is absorbed by the body during the process of digestion. Like other burning processes this one furnishes heat to keep the body warm and in addition it supplies energy for doing work and for muscular movements. For the most part the products of this body "fire" are carbon dioxide and water and these are exhaled from the lungs to which they are delivered by the blood stream.

Uses of Pure Oxygen. The first property of pure oxygen

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Courtesy of the Mine Safety Appliances Company

Fig. 10. Inhalator for Re-establishment of Breathing

which was discovered by Priestley was its ability to cause the flame of a candle to burn with much greater brilliance than is caused by the air. This describes oxygen completely. For every change brought about by the oxygen of the air there is a much more rapid change which is brought about by pure oxygen. Because of this, pure oxygen is put to use in many instances, both in industry and in medical practice.

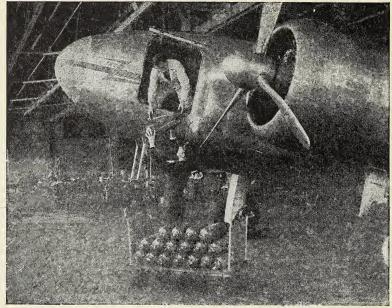
In diseases where the normal capacity of the lungs is impaired (pneumonia) some oxygen is added to the air inhaled by the patient. This is done by means of an "oxygen tent" which covers the head and which is filled with an oxygen-rich atmosphere. Because of the added oxygen, a small amount of lung tissue is made to do more than its normal share of work. Similar methods are employed in the treatment of persons who have inhaled poisonous gases. In the production of anesthesia by nitrous oxide (dentist's gas), or by ethylene, pure oxygen is carefully supplied along with the anesthetic.



Courtesy of the Mine Safety Appliances Company

Fig. 11. The Inhalator Saves a Life

When airplanes fly at great heights the pilots and passengers suffer from "air sickness" unless steps are taken to prevent it. As we go up into the air the amount of oxygen decreases. Strike a match in a transport plane even at 10,000 feet and there is scarcely enough flame to light a cigarette. This lack of oxygen causes a slowing down of the burning processes in the body and as a result, sickness, faintness, and dulling of the senses follow. In spite of this difficulty the engineers keep trying to increase the height at which planes engaged in transcontinental and transoceanic traffic may fly. They claim that they can make the engines function better, attain greater speeds, and travel in smoother air at altitudes from 15,000 to 30,000 feet. Modern warfare has shown that there are times when an altitude of 30,000 feet is quite desirable. One of the obvious remedies for the illness due to flying at such heights is to supply oxygen to the atmosphere which is breathed by the persons in the plane. One method used has been to seal the cabin of the plane and maintain a constant oxygen content from tanks of the gas. This method involves a great many other problems such as the removal of odors, regulation of the moisture content of the air, and the removal of excess carbon dioxide. An-

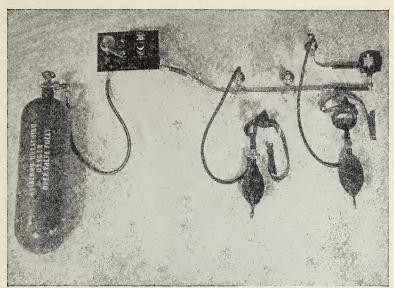


Courtesy of the Northwest Airlines Inc.

Fig. 12. Loading an Experimental Plane with Oxygen for Pilots and Passengers

other method involves the use of small masks which are worn by each person aboard the plane. These masks are not for the purpose of keeping poison gases out but to feed normal amounts of oxygen from a cylinder or bladder. Some of this equipment is shown in the pictures and represents the results of research done by the engineers and doctors of the Mayo Clinic at Rochester, Minnesota.

The use of pure oxygen permits the production of very hot flames. An ordinary gas flame burning in the air may get quite hot but if a supply of pure oxygen is fed to the burner the intensity of the heat is greatly increased. If oxygen were fed into an ordinary furnace in place of air the temperature of the fire would become so great that the iron of the furnace would melt and burn like kindling wood. By means of special burners, gaseous fuels are burned with oxygen in order to give the high temperatures required for welding where a metal is caused to

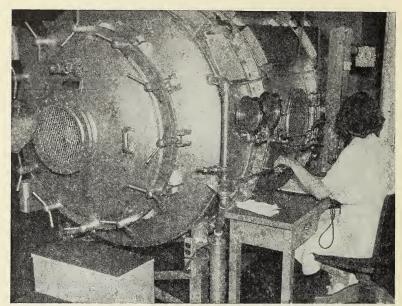


Courtesy of the Northwest Airlines Inc.

Fig. 13. Essential Parts of Oxygen Equipment for Airplanes as Developed by Dr. Boothby and Dr. Lovelace of the Mayo Clinic

melt and run into a crevice between two pieces of metal which are to be joined. If, however, the supply of oxygen is increased beyond that required for burning the fuel, some of the metal will burn. At the temperatures produced by such flames iron will burn in pure oxygen like a highly combustible substance. It is upon this fact that the flame cutting of metals is based. The combustion of the metal itself gives rise to considerable heat and, when once started, it supplies most, if not all, of the fuel for the maintenance of the high temperature.

Production of Pure Oxygen. The industrial uses of pure oxygen are so great that an annual production of over 2,000,-000,000 cubic feet of it which is valued at more than \$20,000,000 occurs in the United States alone. Of this total production about 90 percent is obtained from liquid air by methods which have already been mentioned. Almost all of the remaining amount is produced from water. To do this, an electric current is passed through water which contains a little



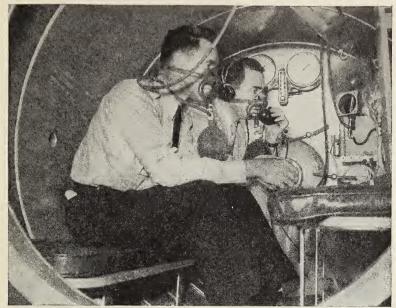
Courtesy of the Northwest Airlines Inc.

Fig. 14. Vacuum Chambers to Simulate Substratosphere Flying Conditions for Experiments at the Mayo Clinic

sulfuric acid or caustic soda. Oxygen collects at the positive electrode while hydrogen collects at the negative electrode. The two gases are kept separated and are put into tanks under pressure.

Small amounts of oxygen may easily be prepared by heating certain compounds. Such methods date back to the work of Priestley and Scheele. The oxygen so prepared costs more than the commercial price and thus the use of such methods is not worth while except for small-scale laboratory use. A few of these are described.

- 1. Mercuric oxide contains 7.38 percent of oxygen and when strongly heated it decomposes to give free mercury and oxygen. Most of the metals will form compounds known as oxides but only a few of them will decompose when heated as does mercuric oxide.
- 2. Barium dioxide contains 18.9 percent of oxygen and when heated to 700° C. it loses half of this as oxygen gas and

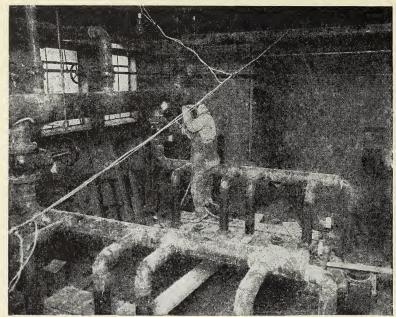


Courtesy of the Northwest Airlines Inc.

Fig. 15. Northwest Airlines Pilot and Dr. Lovelace of Mayo Clinic Wearing Oxygen Equipment in Vacuum Chamber

forms a substance we know as barium oxide. If, then, the barium oxide is heated to 500° C. in the presence of an excess of air it will again unite with additional oxygen to give back the original barium peroxide. This cycle of changes has been used for the commercial production of oxygen from the air.

3. Potassium chlorate contains 39.2 percent of oxygen and if heated to 400° C. it loses all of this oxygen rapidly. The material which is left contains only potassium and chlorine and is known as potassium chloride. It is by this method that oxygen is usually prepared in the laboratory. In actual practice, however, a little manganese dioxide is mixed with the potassium chlorate before heating and as a result the oxygen is liberated at a much lower temperature (about 200° C.). After all of the oxygen has been liberated from the potassium chlorate, the resulting potassium chloride may be dissolved in water and all of the original manganese dioxide recovered by simple

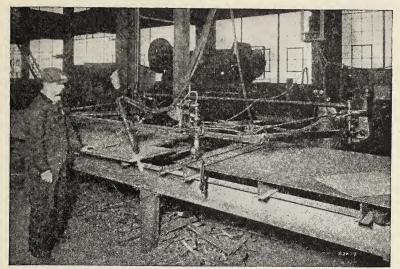


Courtesy of the Air Reduction Sales Company

Fig. 16. Welding 6 inch Pipe Line by Aircowelding Method

filtration through a filter paper. The manganese dioxide is thus a queer sort of chemical helper which makes this change take place more easily. We will have occasion to mention other chemical helpers from time to time and we will classify all of them as *catalysts*.

Chemical Changes. The changes which take place when a substance burns are definite. Some of these changes are easily noticed while others take place without being apparent. The things formed (products) from the burning process are always different from the things which are burned. These differences are noted in composition, energy content, and properties. If a piece of carbon burns, the product is carbon dioxide, formed by the union of the carbon with oxygen, and heat is liberated. Now, carbon dioxide is quite different from either carbon or oxygen in almost all its properties. Such a change is typical of a large number of changes which are termed *chemical changes*.



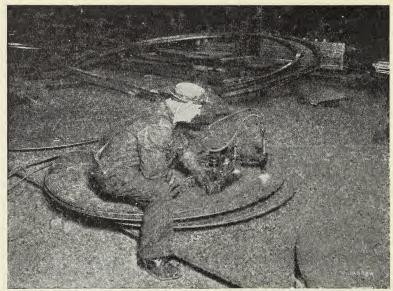
Courtesy of the Air Reduction Sales Company

Fig. 17. Preparing a Steel Plate for Welding with an Oxyacetylene Flame Cutting Machine

One of the most easily recognizable results of a chemical change is a change of energy, and it is frequently by this means that we know a chemical change has taken place. If one steps on the starter switch of a car the engine is turned because of the electrical energy released by a chemical change in the storage battery. This reaction takes place only during the short time that the electrical circuit is complete but a large amount of energy is released. When one strikes a match the energy of the burning process is released both as heat and as light.

Not all chemical changes release energy when they take place since many such changes are known to reverse the process and absorb much energy. For instance, the charging of the storage battery is such a chemical change.

In the light of the discussion given in Chapter 1 it becomes apparent that chemistry is interested in all these changes of the types mentioned. Someone has defined chemistry as the science which deals with the changes in the composition of matter, the energy changes which accompany them, the causes which produce them, and the laws which govern them. It is



Courtesy of the Air Reduction Sales Company

Fig. 18. Flame Cutting Circular Shapes

also apparent that all changes in form which do not involve the other changes listed do not constitute changes of a chemical nature. Thus, the melting of iron, the molding of an article of clay, and other such changes are purely physical and are of no special interest to us while we are dealing wholly with chemistry.1

¹ For Summary and Questions see end of Chapter 5.

THE ATMOSPHERE: ITS COM-PONENTS, CONTINUED

NITROGEN

It was in 1772 that a professor of botany, by the name of Rutherford, discovered the presence of nitrogen in the air. He enclosed air over water in an inverted jar and in it he burned various substances such as carbon and phosphorus. It was observed that the volume of air became smaller and that the residue was different from ordinary air. The experiment was repeated using mice to breathe the air and similar results were obtained. The unused air would no longer support a flame and mice placed in it were unable to live. Rutherford considered it to be air saturated with phlogiston. Lavoisier was the first to recognize this gas as a definite substance and he named it azote (lazy) because it was so inactive. About fifty years later it was given the name nitrogen (niter producer) because it was found to be present in a substance then known as "niter" and which we now call potassium nitrate.

Importance of Nitrogen. The name which Lavoisier gave to nitrogen is quite fitting for this element. While it does take part in the formation of many substances yet most of the nitrogen in the world exists as the free gas. Almost 75 percent of the entire weight of the atmosphere is due to nitrogen. In terms of actual figures we may say that over each square mile of the earth's surface there are approximately 20,000,000 tons of nitrogen. It is fortunate that nitrogen does not have the chemical activity of oxygen and that the oxygen of the air is diluted with this relatively inert gas. If we had to breathe pure oxygen there is no doubt but that we would live much

shorter lives. We would burn up faster. A fire, once started, in an atmosphere of pure oxygen would be most difficult to control and the use of ordinary stoves and furnaces would not be possible. We would also have to use other things than iron and steel in the construction of bridges, buildings, and machinery because pure oxygen would certainly cause them to rust away in a hurry. Wood, too, would suffer rapid decay as would other such material.

In spite of the inactive nature of nitrogen its compounds are of the utmost importance. The very cell structure of our bodies contains compounds of nitrogen which are essential to life. Plants, too, require nitrogen for their growth and it is from them that animals obtain all of their supply. Some plants are able to get their nitrogen directly from the air with the aid of bacteria which live on their roots but this is not generally true. As a rule, the nitrogen of the air is not available to plant life at all. It is because of this that nitrogen fertilizers must be added to the soil.

Ever since the discovery of gunpowder changed the course of warfare the world has sought compounds of nitrogen which are known as nitrates. All explosives which have ever been of any importance have been made from compounds of nitrogen. In the pioneer days of our country it was of prime importance for every settlement to possess a supply of saltpeter (potassium nitrate) with which to make gunpowder. This was aided at times by their saving every bit of animal matter which could be converted into this necessary compound. Later a supply of suitable material was discovered in large deposits in South America and it is known as Chilean nitrate. From this, the necessary nitrogen compounds may be obtained and for many years the wartime defense of all countries was dependent upon this South American supply which is essentially sodium nitrate. With a world full of nitrogen all about them they were unable to use it as a fertilizer or for explosives just because they did not know how to make it unite chemically with anything else which could be economically used.

Since about 1913, however, it has been possible to manu-

facture suitable compounds of nitrogen from the nitrogen of the air. This has made available an unlimited supply of explosives and fertilizers and there is no doubt but what it has made possible many of the horrors of modern war. The country that wants to go to war no longer has to look to the sea lanes for a source of explosives because all the nitrogen needed will drift in on the wind. They need only mechanical power to make use of it since heat and pressure are required to cause nitrogen to combine with some other elements. The industry is large enough to supply nitrogen fertilizers even in time of war. The details of the processes used will be given along with the discussions of fertilizers and explosives since the reader is not ready to understand the chemistry involved at the present time.

OTHER COMPONENTS OF THE ATMOSPHERE

Water Vapor. It is common knowledge that the air contains water vapor at all times. The amount present depends upon many factors such as location, temperature, wind currents, altitude, and other things which seem to affect the weather. If we are hot and sticky in the summer we blame it on the moisture of the air and if we are cold and uncomfortable in the winter in spite of clothing we again blame it on the moisture content of the air. If a wind blows which dries the farm crops and burns the skin we complain, and if the days are full of fog and the nights cause us to speak with husky voices we again complain. Always we find fault with the water vapor in the air. We are taught from the time of our grade schools that rains are produced by the proper combination of moisture-laden air currents. Our whole lives are regulated by the presence or absence of such a small amount of this vital substance. The exact treatment of water vapor will appear under the discussion of water.

Carbon Dioxide. When fires burn there are great quantities of carbon dioxide formed which are at once given to the air. Every creature that breathes exhales carbon dioxide as one of the products of respiration. It is evolved during the process of

decay. One may be tempted to think that the total quantity of this gas in the atmosphere is constantly increasing, but nature has provided a balance. All plants which we commonly know depend upon the carbon dioxide of the air for their growth. Every tree and blade of grass stretches forth its green leaves into the air in order to have access to as much of this life-giving substance as is possible. Because of this use of carbon dioxide we find that its amount in the atmosphere remains fairly constant (.03 to .04 percent).

The leaves of the plants serve as manufacturing establishments where the carbon dioxide of the air and the water within the plant may be brought together and made to form starch, sugar, cellulose, and other plant tissue. The energy for these changes comes from the rays of the sun and the green chlorophyll within the plant acts as a chemical helper or catalyst.

Carbon dioxide has a place in the family kitchen. We have often heard that bread is the staff of life but when we buy or make bread we want it to be filled with little holes. We know that the bread has been made to rise prior to baking and it is to carbon dioxide that we look for this action. Sometimes the cook places baking powder in the dough and sometimes it is baking soda but in any case carbon dioxide is released throughout the dough and the form of the bubbles is retained by the baking process. Frequently the carbon dioxide is formed within the dough by the fermenting action of yeast on the starch and sugar which are present.

The preparation of soft drinks and other beverages which contain carbon dioxide is classed as big business. The drinks so prepared are effervescent and have a taste which is enjoyed by almost everyone. As a rule, these carbonated drinks are prepared by the addition of sugar syrup, flavoring, and coloring matter to water and then when thoroughly cool the liquid is treated with carbon dioxide under pressure. So long as the mixture is kept cold the gas stays dissolved but if the bottle is opened while warm most of the carbon dioxide escapes.

Within recent years we have become acquainted with "dry ice." When carbon dioxide is put under pressure and cooled

it quickly changes to a liquid. If this liquid is allowed to stream through a small opening into an insulated box a great amount of it is cooled enough to form a white solid. This process is similar to the production of liquid air. The white solid looks like snow and if pressed into a cake it may be handled like ice. It must be remembered, however, that solid carbon dioxide has a temperature which is almost 80 centigrade degrees colder than water ice. Because of this it should never be handled with the bare hands. There are a number of advantages of dry ice over ordinary ice. Many foods must be kept cold during shipment and for this purpose many tons of ice must be placed in the railway cars which serve as refrigerators. If the temperature must be kept very low it is necessary to add a ton or so of salt to the ice. With solid carbon dioxide, however, it is only necessary to use a thousand pounds or so and it is never necessary to add any salt. The saving in freight alone becomes considerable. When water ice melts it forms a liquid which must be disposed of and if salt is also present the liquid causes rust to form in the metal containers. When dry ice is allowed to stand it forms a gas and there is no liquid at all. This means that paper cartons can be used for packages and the entire handling process is kept much cleaner.

There are two main sources of commercial carbon dioxide; the burning of coke and the fermentation industries. The carbon dioxide in the air is in quantities too small to make its recovery worth while. A good grade of coke, which is largely carbon, is burned in an excess of air and the escaping gases are bubbled through water which contains washing soda (sodium carbonate). The carbon dioxide reacts with the sodium carbonate and changes it to sodium bicarbonate which is the same as baking soda. This is crystallized out from the water solution and heated to give back the pure carbon dioxide and the original washing soda which is used over again. The fermentation industries include the manufacture of beer, alcohol, and certain other things which are produced by the action of certain forms of yeast upon starch or molasses. The weight of the carbon dioxide produced is almost equal to that of the

alcohol formed. Regardless of the source of the carbon dioxide it is purified and compressed, with cooling, to a little more than 1000 pounds pressure per square inch in order to change it to a liquid. It may then be put in steel tanks for sale or converted to the solid and sold as "dry ice."

Argon. Soon after the discovery of oxygen and nitrogen, an Englishman, by the name of Cavendish, did a number of experiments in which he passed an electric spark, from a static machine, through mixtures of these two gases. He found that they combined to form an oxide of nitrogen which could be absorbed by the water. Each time he tried the experiment he noticed that a part of the gas was unchanged and further sparking with fresh oxygen failed to cause its combination. He was of the opinion that this small residue of gas (1/120 of the original air) was not nitrogen and he made his observations known through the scientific literature of the time. For more than one hundred years this information went unexplained and probably unnoticed.

In 1894, another Englishman, Lord Rayleigh, was interested in the weights of various gases. Among others he weighed nitrogen and in the true scientific spirit he prepared his nitrogen samples by every possible method. Some of these were prepared by burning all the oxygen out of the air and absorbing the products of the combustion with suitable agents and some of them were prepared by the decomposition of substances which liberate nitrogen when heated. You may imagine his surprise when he found that he could not weigh the two and get similar results. He checked his balances and checked his methods only to find that he was introducing no error. The gas from the two sources could not be the same. The gas prepared from pure compounds of nitrogen was lighter than the gas prepared from the air.

Sir William Ramsay was called in to help him on the problem and together they found references to the earlier work of Cavendish. They then passed the nitrogen produced from the air over white-hot magnesium and this formed a solid compound, magnesium nitride, with the nitrogen. They found about 1/108 of the original volume of the air refused to combine with the magnesium. They agreed that it must be a new substance and they called it the element *argon*. This is the Greek for "lazy" and they so named it because of its inactivity. Up to the present time no one has been able to make argon combine with any other element or substance. It is now thought to be entirely inactive.

Even though there are no compounds of argon, it finds a use. By using care in the liquefaction of air they are able to separate it as a by-product. In the manufacture of electric light bulbs it has been found that those filled with this argon give much better service than those which are evacuated or which contain any other gas. As a result, most of the bulbs larger than fifty watts are filled with argon.

Helium. During a solar eclipse in 1868, Sir Norman Lockyer observed the presence of a peculiar yellow color in the light from the sun. Now white light is really a mixture of all the various colors and by sending the white light through suitable glass prisms it is possible to separate these colors into a rainbowlike spectrum. If this spectrum is spread out enough the different colors are broken up into separate bright lines so that the various shades of the same color are divided one from the other. During the course of investigations it had been found that by heating various elements to a white-heat they would give rise to certain characteristic sets of these colors. Each element was found to be peculiar unto itself so that by observing the colors of light given off by hot substances the investigators were able to identify the elements in the heated material. It was with all of this information that Lockyer approached the task of observing the light given off by the layer of gases surrounding the sun. He found a yellow line in the spectrum of the sun which had never been produced by heating any known element. He then made the simple assumption that there must be a gaseous element on the sun which had, at that time, never been encountered on the earth. To this element he gave the name helium, meaning "the sun."

Soon after 1890, an American chemist, W. F. Hillebrand,

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who was working with the U. S. Geological Survey, heated a mineral known as cleveite and from it got an inactive gas which he described as nitrogen. By this time, Ramsay was looking for compounds of argon and he passed up no opportunities to analyze all samples of inactive gases which he could find. The discovery of argon had taught him an important lesson. He at once got hold of all the samples of cleveite which he could find, heated them, and collected the gases which were evolved. By means of white-hot magnesium again he removed all of the nitrogen and still had some gas left. This, he heated to incandescence so that he could observe the colors emitted and possibly identify it. The gas proved to be helium. Like argon it was found to be entirely inactive and formed no compounds whatever. It was found to be much lighter than air and next to hydrogen it is the lightest gas known.

Helium took on importance almost at once. Men had been going up into the air in balloons of various types and the most effective lifting gas was hydrogen. The trouble was that this same hydrogen was extremely explosive when in contact with air and there was a constant danger of fire. The possibility of getting helium for filling observation balloons for the defense of the British Isles was considered. This element is present in the air to the extent of 0.0005 percent by volume and it would take 200,000 cubic feet of air to supply one cubic foot of it. Some helium has been prepared from air by the careful evaporation of liquid air but the cost prohibits its use for quantity production.

A gas well was discovered at Dexter, Kansas, about 1907 and during the proper celebration attempts were made to light it. The gas failed to light, however, because it contained too much nitrogen. A sample was sent to Dr. Cady, at the University of Kansas, for analysis. It just happened that Dr. Cady had done some of the early work on helium and he went about the task with the proper methods. He got rid of all the combustible material, then all of the nitrogen, and still had some gas left. This contained an amount of helium equivalent to almost two percent of the original gas used. Samples of natural gas from

all over the country were collected and their helium content determined. It was discovered that the quantity of this element present depends upon the geographical location of the well and the experimenters were able to predict the helium content of a sample of gas without actually making the determination. By the time this work was nearing completion the first world war was started and the Allies were wanting Dr. Cady to start a plant for the production of this valuable gas. By this time the Kansas gas was exhausted and other sources were looked for. A plant was erected in Texas where the gas contained almost one percent of helium and now there is a large plant at Amarillo, Texas, which produces more than 20,000,000 cubic feet of this gas each year when working at full capacity. The first helium produced sold at the rate of \$2500 per cubic foot but now the commercial price is within the range of \$8.00 to \$15.00 per thousand cubic feet.

Because of the importance which helium has attained, the government has taken over all available supplies and it is now operated as a monopoly. By an act of Congress this gas may be sold for medical, scientific, and commercial purposes at reasonable prices. Sales of large amounts to foreign powers have been refused.

A mixture of helium and oxygen is used in place of air for divers and others who must work under high pressure. When digging tunnels under rivers the men must work in compressed air. This causes more than the ordinary amount of air to dissolve in their blood and when they return to the surface the nitrogen comes out and forms bubbles in the blood stream. The men so affected appear to be drunk and sometimes they die from the effects. A person so affected is said to have the "bends." The Bureau of Mines working with the Public Health Service has found that the helium-oxygen mixture permits them to bring a man to the surface much faster than is possible when air is used.

Helium is twice as heavy as hydrogen but it is so much lighter than air that it has a lifting power which is 92 percent that of hydrogen. It is possible, also, to use a mixture of 20

percent of hydrogen and 80 percent of helium without danger of its catching fire. A number of large airship accidents have occured within the memory of most of us and many were caused by the hydrogen with which the balloons were filled. The greatest disaster of all time which these ships experienced was that which befell the great German ship Hindenburg when it caught fire and burned while making a landing at Lakehurst. This was a passenger liner and had covered countless miles in use between Europe and the Americas. The United States has filled its balloons with helium but even they have experienced difficulty. Two of these massive ships were broken apart in storms but in neither case was the accident followed by fire.

Neon, Krypton, Xenon. From the time of the discovery of argon and helium in the atmosphere, Ramsay began to suspect that there were other inactive gases present in small amounts. By the most careful boiling of liquid air, followed by lique-faction and reboiling of the separate gases he and his helpers were able to identify three other elements. These were named neon (new), krypton (hidden), and xenon (stranger). Of these, we are probably more accustomed to the behavior of neon than of any other. When placed under small pressure in a tube fitted with electrical connections we get the familiar neon sign. Argon and helium are sometimes mixed with neon for these signs in order to get the desired color effects. The color of the glass tube influences the color of the light given off as does also the presence of certain types of luminous paint. This phenomenon is discussed on page 182.

Relative Abundance of Atmospheric Gases. There is a slight variation in the composition of the atmosphere when sampled at different locations. The relative quantities of the

gases in the atmosphere are as follows:

Nitrogen1	volume in 1.28 volumes of air
	volume in 4.8 volumes of air
	volume in 106.8 volumes of air
	volume in 3,400 volumes of air
	volume in 10,000 volumes of air
	volume in 65,000 volumes of air

Helium1	volume in	200,000 volumes of air
Krypton1	volume in	1,000,000 volumes of air
Xenon1	volume in	11,000,000 volumes of air

SUMMARY

The atmosphere is a mixture of a number of gases. Those which directly affect us are nitrogen, oxygen, carbon dioxide, and water vapor. The components of the air may be separated by means of liquefaction brought about by the application of pressure with cooling.

For animals and other forms of life with respiratory systems the oxygen is essential to carry on the "burning" of foods within the tissues of the body. Oxygen takes part in rusting, decay, and the burning of fuels. Hot flames may be produced by burning gaseous fuels with pure oxygen using special burners. Oxygen is used in the treatment of pneumonia, while giving certain anesthetics, in mine rescue work, and to supply passengers and crews in airplanes flying at great heights.

passengers and crews in airplanes flying at great heights.

Most of the oxygen used is prepared from liquid air and a small amount is prepared from water by the use of an electric current. Small amounts of oxygen may be prepared by heating certain compounds of oxygen which are decomposed by heat.

The nitrogen of the air seems to have no particular use except to dilute the oxygen and thus prevent too rapid burning. Compounds of nitrogen are essential to plant and animal life but neither is able to take nitrogen from the air and use it. Chilean nitrate has served as the main source of nitrogen compounds until twenty-five years ago. Compounds may now be made from the nitrogen of the air and these serve as the starting material for the manufacture of fertilizers and explosives.

Chemical changes are those during which new substances are formed having different properties and different energy contents than the original material.

There are five completely inert gases in the atmosphere. Argon finds use in filling light bulbs. Helium is extra light and noninflammable and is used to fill airships. It is separated from natural gas. Neon is used in electric signs. Krypton and xenon have no particular uses as yet.

REVIEW QUESTIONS

- 1. Give two independent pieces of evidence which show air to be a mixture.
- 2. What were the contributions of Priestley, Scheele, and Lavoisier to the early history of oxygen?

3. In what way did Mayow explain combustion?

- 4. Why did Priestley call the gas he prepared "dephlogisticated air"?
- 5. Give the differences between the phlogiston theory and the modern theory of combustion.

6. By what means does a fish get oxygen for respiration?

7. Breathing becomes quite difficult in air which contains as little as 16 percent of oxygen. Would you conclude that the body uses all of the oxygen in the air which is taken into the lungs?

8. It is an easily observed fact that faintly moist material decays faster than dry material, moist iron rusts more rapidly than dry iron, and barely moist hay is more apt to take fire spontaneously than dry hay. What sort of agent does the trace of moisture appear to be?

9. What sort of change is it which produces a new substance

and an energy change?

10. What are the ideal conditions for the production of spontaneous combustion?

11. What part do the red blood corpuscles play in respiration?

12. Why is oxygen sometimes added to the air breathed by pneumonia patients?

13. Why is extra oxygen supplied to persons in airplanes flying

at great heights?

- 14. What happens when white-hot iron is placed in a stream of pure oxygen?
 - 15. Describe the method of getting pure oxygen from the air.
- 16. Name some compounds from which oxygen may be prepared by heating. Why are these not commercial sources?

17. List as many cases as you can which show the destructive action of the gases in the atmosphere.

- 18. Define the field of chemistry.
- 19. Why must animals eat compounds of nitrogen? What is the source of these?
- 20. Why are nitrogen compounds essential to warfare? Where does the nitrogen for these come from?
- 21. Why are countries no longer dependent upon the nitrates from Chile?
- 22. What is the meaning of the name which Lavoisier gave to the gas which we call nitrogen? Why was this name especially suitable?
 - 23. What is the chief function of atmospheric nitrogen?
 - 24. What are the principal products produced by respiration?
 - 25. What use do plants make of carbon dioxide?
- 26. What use is made of carbon dioxide in the family kitchen? In beverages?
- 27. What is dry ice and how is it made? What are the advantages of its use?
- 28. What indication did Cavendish have for the presence of argon in the air?
- 29. Why did Lord Rayleigh suspect the presence of a new substance in the air? How was its presence shown?
- 30. Why was it possible to detect the presence of helium on the sun before it was found on the earth?
- 31. Why did Hillebrand assume the gas he obtained from cleveite to be nitrogen?
- 32. Why should the Government have a monopoly on helium production?
- 33. What uses has helium? Why is helium used in place of other gases?
- 34. Why is helium not produced from the air in those countries that have no supply in natural gas?

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WATER: ITS COMPOSITION. ATOMIC THEORY. UNITS OF MEASURE

We can be certain that the first man to inhabit the earth was acquainted with water. Its presence was considered as essential to life and we may recall that Aristotle listed it as one of the four primary elements of which all things are composed. One may readily see that an accepted concept of this sort could stifle thought for some time but it is hard to believe that it could do so for two thousand years.

Synthesis of Water. Among the various things done by Cavendish was the addition of an acid to bits of zinc which resulted in the evolution of a gas. There is evidence, too, that Boyle had done this same thing almost one hundred years previously. Cavendish, however, was not satisfied only to have prepared this gas and he set about to discover how it would behave under various conditions of treatment. It did not take him long to discover that it would burn if ignited in the air. After the discovery of oxygen had been announced he mixed his new gas with oxygen and set fire to the mixture with a spark from a static machine. An explosion took place and a small amount of liquid formed. This liquid was identified by him as water. He assumed the new gas to be a form of phlogiston and he named it "inflammable air."

With his usual keen ability, Lavoisier took up the work where Cavendish left off and he demonstrated the relationship between "inflammable air," oxygen, and water. This was merely another bit of evidence for his theory of combustion and the "inflammable air" was a new element. This he named bydrogen (water producer). It was shown that a stream of

hydrogen will burn in the air very much as we know a stream of gas burns if lighted at the stove. The flame produced by hydrogen is much hotter than an ordinary flame and the only product of the combustion is water vapor. This union of hydrogen and oxygen is classed as a chemical change since their combination produces a new substance with properties which are different from those of the uniting substances, and during the combination energy is evolved. Such a formation of a new substance from the elements or from more simple things is called synthesis.

Decomposition of Water. It was not long after the true composition of water was demonstrated before men began their attempts to bring about its decomposition into the elements. This was materially aided by the discovery of the ordinary electric battery in 1799, when for the first time in history scientists were supplied with current electricity. This new tool was destined to become one of the most important in scientific research. Early in 1800, two English workers, Nicholson and Carlisle, reported that they had passed this new current through water which contained a little acid. They had obtained hydrogen at one wire and oxygen at the other. These gases had bubbled up through the liquid and had been trapped in tubes.

Quantitative Composition of Water. With the definite knowledge concerning the composition of water there came the desire on the part of investigators to determine the exact relationship between the amounts of hydrogen and oxygen which are combined in it. This has been done by means of two methods: synthesis and decomposition.

The outstanding work on the exact composition of water as determined by synthesis was done by Morley, an American chemist. He weighed the amounts of hydrogen and oxygen which combined and then he weighed the quantity of water produced. Because of the number of experiments performed together with the painstaking methods which he used, his work has become an example of accuracy in experimental methods. He was able to show that by weight 1 part of hydrogen com-

bines with 7.94 parts of oxygen and by volume 2.0024 parts of hydrogen combine with 1 part of oxygen.

The decomposition of water by the electric current (electrolysis) has been carried out in an apparatus which permits the measurement of the gases evolved (Figure 19). The ox-

ygen is released at the positive electrode (wire connected to the positive side of the battery) and the hydrogen is released at the negative electrode. The gases rise in the separate tubes and may be measured as they collect. In a large number of experiments it has been determined that the volume of hydrogen obtained is almost exactly twice the volume of the oxygen collected. In fact, if we consider that the two gases do not obey exactly the gas laws, and we make the necessary corrections, we find that by volume the ratio of hydrogen to oxygen is exactly two to one. Regardless of the source of the water used this ratio always is the same.

The Conservation of Energy. During the formation of water from hydrogen and oxygen by burning we find a considerable amount of energy released

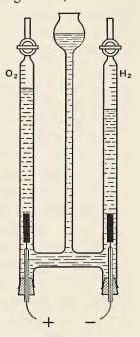


Fig. 19. The Electrolysis of Water

in the form of heat. In a number of experiments in which exactly the same weights of water are produced we find that exactly like amounts of heat are liberated. Also, it has been determined that exactly equal amounts of electricity are required for the decomposition of like amounts of water.

The changes involved during the synthesis and the decomposition of water may be represented as follows:

hydrogen + oxygen \rightarrow water + heat energy + electrical energy → hydrogen + oxygen water

The arrow used in these expressions and which will be used in other examples may be read to mean "gives." The two expressions as written tell something about what happens but there is no indication of how much of each substance is involved or how much heat or electrical energy is connected with each change. Now without information to the contrary it seems safe to assume that the energy content of all water is the same if we take equal quantities and have them under similar conditions of temperature. In the same way we hope that the energy content of all like samples of hydrogen are the same, and of all like samples of oxygen are the same. If these things are true, then in some way the heat given off when oxygen and hydrogen combine should be equivalent to the electrical energy required to decompose a like amount of water. This supposition is in reality a statement of a fundamental law of nature. This is the law of the Conservation of Energy which states that energy can neither be created nor destroyed. We know that heat may be converted to work, work may be converted to electrical energy, and electrical energy may be converted back to heat again but we also know that there are certain losses at each step. We do not suppose that we can retain every bit of energy as it goes from one form to another but we are sure that the losses are due to the inefficiencies of the processes used. The energy losses are usually dissipated to the atmosphere in the form of heat.

THE CONCEPT OF ATOMS

During the last third of the eighteenth century the exact methods of science as applied to chemistry began to take form. When it was found that two substances would enter into chemical combination the question was at once presented as to the relative amounts of each involved. In the preceding section we have mentioned some of the work which was begun by Cavendish but was not completed until near the end of the nineteenth century when Morley published the results of his experiments. Cavendish also caused nitrogen and oxygen to

unite by means of energy supplied by the spark from a static machine. Always he found that the amounts of nitrogen and oxygen which combined had a definite relation to each other.

Data dealing with the quantitative relationships between reacting substances began to pile up in the laboratories of several investigators. It must be remembered that this collection of abundant data constitutes the first step in what we call the scientific method. From the great number of known facts one would expect certain capable workers to point out similarities and to state natural laws. After the statement and proof of the laws it then would be possible to express theories in an attempt to explain the laws and the observed facts. Only time can permit the collection of enough data to bring about the acceptance or rejection of the theories.

Without going into detail as to how all of the facts were obtained we can observe clearly some of the thinking, planning, and experimentation that have moved us forward to our

present explanations.

Definite Composition of Compounds. It has already been pointed out that pure water, from whatever source, always has the same composition. This has been extended and found to be true for all other pure substances which are considered as compounds (things that contain two or more elements chemically united). This has become known as the Law of Definite Composition which states that the composition of a pure compound is always the same regardless of where it may be obtained.

Multiple Proportions. In 1803, John Dalton, an English school teacher, pointed out the fact that sometimes two elements could combine in more than one way to form more than one compound if the conditions were changed properly. For instance, there are three separate and distinct oxides of nitrogen which are gases. These are known as nitrous oxide, nitric oxide, and nitrogen dioxide and the one which is formed depends entirely upon the method employed for its preparation. This sort of thing is not confined to oxygen and nitrogen but is found to be true for many other pairs of elements. Upon care-

ful examination it is found that an unusual relationship exists between the amounts of the two elements present in the various compounds of such a series. Thus, in nitrous oxide the weight of nitrogen is to the weight of the oxygen as 14 is to 8, while in nitric oxide the ratio is 14 parts by weight of nitrogen to 16 parts by weight of oxygen, and in nitrogen dioxide 14 parts by weight of nitrogen is combined with 32 parts by weight of oxygen. In this example the amount of nitrogen used for comparison was taken as the same in each case and the quantity of oxygen combined with it was determined. It will be noticed that the amounts of oxygen in the three cases are multiples of 8. Such facts led to a statement of the Law of Multiple Proportions as follows: If two elements form more than one compound, the weights of the one which combine with a fixed weight of the other can be represented by a ratio of small whole numbers. In the example which has just been given we may see that this ratio is expressed as 1:2:4.

The Conservation of Matter. Certain of the Greek philosophers believed that no part of matter is destroyed during the process of being converted into other forms. It seems strange to the reader of today that this idea was not generally accepted until after 1785 and that most of the time it was not accepted by anyone. It has been mentioned that Lavoisier experimented with combustion and other chemical changes and it was during these experiments that he demonstrated the truth of the above statement. He proved that the sum of the weights of all the substances which react together in a chemical change is numerically equal to the sum of the weights of all the substances produced during the change. This fact as stated constitutes the Law of the Conservation of Matter. The results of thousands of experiments which have been performed by many workers through the years bear out the truth of this law. If there is any change in the total amount of matter during a chemical change it is too small to be detected by the most sensitive methods of weighing.

Atomic Theory. As additional experimental facts accumulated it was possible for scientists to formulate more definite

ideas concerning the nature of matter. Dalton had conducted a number of experimental studies and in the light of the evidence he obtained he announced the atomic theory. For one to say that only Dalton thought of this conception of matter would be entirely incorrect, since a Greek philosopher presented such an idea nearly 3000 years ago. The early theories, however, were entirely lacking in definiteness and were products of pure thought alone with no quantitative data to support them. Later Robert Boyle and Isaac Newton revived this atomic concept of matter but they, too, could deal only in generalities, since at that time the Law of Definite Composition was not considered as valid. To Dalton, the greatest evidence lay in the Law of Multiple Proportions which he had outlined a year earlier.

The more important points of Dalton's atomic theory may be summarized as follows:

- 1. All substances consist of small particles called atoms which are indivisible.
- 2. All the atoms of any one substance are alike in size and weight.
 - 3. Combinations of elements take place between atoms.
- 4. The "compound atom" (the unit of a compound) is always made up of a definite number of each kind of atom of which it is composed. This compound atom is now called the molecule.
- 5. The atoms of two elements may combine in different' ratios to form more than one compound.

The laws of definite composition and of multiple proportions are easily explained on the basis of this theory. If the molecules of a compound are always made up of a definite number of each kind of atom of which the substance is composed, and if all the atoms of a given element are alike in weight, then it must follow that the proportion by weight of each constituent element of a compound is constant. This theory, therefore, satisfactorily explains the law of definite composition.

If we assume that two elements may react together in more

than one proportion, without our trying to explain why, this theory will be of great use. Suppose that one atom of the first element may react with one atom of the second element to form one compound and then suppose that under some other conditions one atom of the first will combine with two atoms of the second to form another compound. Let us write this as we did the formation of water but let us call the two elements A and B. We have the two cases:

$$A + B \rightarrow AB$$

 $A + 2B \rightarrow AB_2$

The subscript indicates the number of atoms of B which are contained in a molecule of the second compound. In each case the amount of the element A is the same but the amount of B in AB_2 is twice as great as in AB. This then is just what the law of multiple proportions expresses. The weights of the one element which combine with a fixed weight of the other can be represented by a ratio of small whole numbers. The weights of element B which are combined with a fixed weight of element A can be expressed by the ratio of 1:2. If the compound AB_3 is formed the same reasoning may be applied successfully.

Errors in Dalton's Theory. While the theory of Dalton did much to clarify scientific thinking, and is still of much use to-day, yet errors and misfit facts were bound to appear. Progress is attained only to the extent that we are able to modify the ideas of earlier workers but modifying another man's theory does not mean that you abolish it or wipe it out as no good. Dalton's approach was from one viewpoint only and he made his scientific picture accurately to fit what he saw. One can compare his approach to that of a person who sees a house from the front only and then describes the entire house from the part that he sees. Naturally there are many things left to be described if other people go all around and inside the house. So it has been with atoms. Some of the later knowledge is pointed out here in order to give an idea of the modifications but each of these items must be discussed at some length later.

1. All the atoms of an element are not identical but the

mixture found in nature is usually the same everywhere. We have heavy hydrogen and light hydrogen but wherever hydrogen is found the relative amounts of the two are the same.

2. Atoms can be decomposed. Dalton never heard nor did he dream of atomic disintegrations by electrical means as may be brought about with our modern "atom-smashers."

3. Dalton did not distinguish between atoms and molecules because here, too, he had no knowledge.

UNITS OF MEASUREMENT

In any discussion involving measurements it becomes necessary to adopt some standard so that the things measured may be compared. We are accustomed to common units of measure such as the pound, ton, bushel, gallon, quart, foot, yard, horsepower, and kilowatt. These are a part of an unrelated hodgepodge system which has been in general use in this country. Regardless of the lack of relationship between these common units we are aware of a certain quantity which goes with each of them. The field of chemistry is not peculiar to any one country and this requires that an international system of units be used. The early scientific workers were aware of the situation and through the years a system of planned interrelated units grew into being. Because this system was allowed to grow, instead of being invented and thrust full blown upon the scientific world, it has lived and is equally useful in all nations.

From the viewpoint of chemistry we are interested in units for the measurement of temperature, pressure, time, length, volume, and weight. In addition there are other units which from time to time are useful to the chemist. Among these are the units of heat and electricity. We have already discussed the measurement of temperature and pressure and the unit of time is well known to us all. The units of heat and electricity will be introduced at a later time when they will have more meaning for us.

The Decimal System. The logical and convenient decimal

system of weights and measures was originated in France and was adopted by the French in 1799. After 1820 its use in that country was made compulsory. Since then it has become official or semi-official all over the world. It is known as the metric system.

The basic unit of length, the meter, was originally intended to represent one ten millionth of the distance through Paris from the equator to the North Pole. This unit of length was marked off on a certain bar of durable metal. It later turned out that the calculations were in error — that the distance from the equator to the pole is not exactly what they thought — but the unit was not changed.

The unit of volume, the liter, was originally taken as a cube with sides of one tenth meter (decimeter). Difficulty arose in the measurement of this distance under some conditions and the definition of the unit was changed so that it would be more easily reproduced. In 1901, the liter became defined as the volume of one kilogram of water taken at 4° C. and at average sea level pressure. A slight error was made in the determination of the weight of water and the two definitions of the liter

give slightly different volumes.

The unit for the measurement of weight is in reality a unit of mass. Weight is a property of things in general which depends upon the pull of gravity. At different distances from the center of the earth this pull of gravity varies and thus could not be used as a standard. By making a standard piece of material and comparing everything else with it we will not be bothered with the distance from the center of the earth. If we put the standard object on one arm of a balance and the object to be compared on the other arm then the gravity pull will be relatively the same on each. The amount of material, or matter as some would say, in the standard object is constant regardless of where one takes it, but the pull of gravity on this object will change. The standard of mass is the kilogram and represents the mass of a piece of durable metal which was prepared in France in 1799.

If you were called upon to measure the diameter of a ten-

cent piece, or of a sewing needle, you would hardly want to use a yardstick and state the distances as fractions of this unit. A similar situation would be true if you used a meter stick because the meter is a little longer than the yard. To get away from this difficulty an agreement was reached, about 1870, whereby the one hundreth part of the meter (the centimeter) and the one thousandth part of the kilogram (the gram) together with the second of time were made the practical standards. These three are usually referred to as the C.G.S. system of measurement.

The relationships between various units are given below.

LINEAR MEASURE

1 meter = 100 centimeters = 39.37 inches 1 decimeter = 10 centimeters = 3.937 inches 1 centimeter = 10 millimeters = .3937 inch 1 inch = 2.54 centimeters = 25.4 millimeters 1 mile = 1609.33 meters = 1.60933 kilometers

VOLUME MEASURE

1 liter = 1000 cubic centimeters (almost exactly) = 1.0567 quarts
1 cubic centimeter = a cube 1 centimeter on an edge
1 quart = .9464 liters = 946.4 cubic centimeters
1 gallon = 3.785 liters

MASS (WEIGHT) MEASURE

1 kilogram = 1000 grams = 2.205 pounds 1 gram = 10 decigrams = 100 centigrams = 1000 milligrams 1000 kilograms = 2205 pounds = 1 long ton 1 pound = 453.6 grams

TEMPERATURE MEASURE

0° Centigrade = 32° Fahrenheit = freezing point of water 100° Centigrade = 212° Fahrenheit = boiling point of water 1 Centigrade degree = 9/5 of a Fahrenheit degree Temperature in C.° = (Temperature in F.° – 32) \times 5/9 Temperature in F.° = (Temperature in C.° \times 9/5) + 32

TIME MEASURE

1 second = 1/86400 of the mean solar day

The mean solar day is the average time between two successive crossings of a given meridian by the center of the sun's disk.

PRESSURE MEASURE

1 atmosphere — average pressure of atmosphere at average sea level

- = pressure of column of mercury 760 millimeters high
- = 14.696 pounds per square inch = 2116.32 pounds per square foot.

SUMMARY

The synthesis of water by the union of hydrogen and oxygen was accomplished by Cavendish who called hydrogen "inflammable air."

Lavoisier explained the combustion of hydrogen with oxygen and gave the present name to hydrogen.

Water was decomposed by current electricity, in 1800, and the two gases, hydrogen and oxygen, were obtained from it.

The quantitative composition of water has been studied by methods of synthesis and decomposition. The relative amounts of hydrogen and oxygen combined in water are constant.

The heat given off by the formation of water is equivalent to the electrical energy required to decompose a like amount of water. Energy can neither be created nor destroyed.

The composition of a pure compound is always exactly the same.

When two elements combine to form more than one compound, the weights of one element which combine with a fixed weight of the other element are related to each other as are small whole numbers.

The sum of the weights of all substances which react together is equal to the sum of the weights of all of the products formed during the reaction.

John Dalton proposed the theory that all substances are

made up of atoms which are indivisible and that chemical changes take place between atoms. He explained the three statements given above on this basis. In the light of present day knowledge there are some errors in Dalton's ideas but his fundamental statements still are considered as probable.

REVIEW QUESTIONS

- 1. Who discovered hydrogen? Who named it? Give the meaning of the name.
- 2. What happens when a mixture of hydrogen and oxygen is exposed to a spark or flame?
 - 3. Give a method for the decomposition of water.
- 4. By what two methods has the composition of water been studied?
- 5. State the law of conservation of energy. Explain what it means.
- 6. Substantiate the statement that matter is discontinuous rather than continuous.
- 7. State the laws of: definite composition, conservation of matter, multiple proportions.
 - 8. Summarize Dalton's atomic theory.
- 9. With the aid of the atomic theory explain the laws listed under question 7.
 - 10. Cite some errors in Dalton's theory.
- 11. Express your height in centimeters; your weight in kilograms.
- 12. How many liters of gasoline would be required to fill an 18 gallon tank?

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WATER: ITS COMPOSITION, CONTINUED

THE RELATION OF ATOMS TO MOLECULES

Combining Volumes of Gases. At the time Dalton's atomic theory was suggested no one seemed to have any conception of the relation between atoms and molecules but the experimental work of the next few years supplied information which helped to bring order out of confusion. It has been pointed out that water was found to give two volumes of hydrogen to one volume of oxygen when decomposed by the electric current and that these two gases will combine in this same ratio again to form water if their mixture is ignited by a spark or flame. Gay-Lussac became interested in this bit of experimental evidence, and he carried it much further. The reacting gases were heated above 100° C. before they were made to combine and then the resulting water was kept at the same temperature in order that it would remain as the gas (steam). It was found that the volume of the steam was the same as the volume of the hydrogen which was used and the volume of the oxygen seemed to have disappeared entirely.

This peculiar behavior could not be disputed, but neither could it be explained. Gay-Lussac made many other combinations of gases to see if they, too, behaved like hydrogen and oxygen and he found that they did. Other examples studied included the union of nitrogen and oxygen to form nitrous oxide, of hydrogen and chlorine to form hydrochloric acid, and of nitrogen and hydrogen to form ammonia. The information which was obtained may be represented as follows:

1 vol. oxygen + 2 vols. hydrogen \rightarrow 2 vols. water vapor (steam) 1 vol. oxygen + 2 vols. nitrogen \rightarrow 2 vols. nitrous oxide

1 vol. hydrogen + 1 vol. chlorine \rightarrow 2 vols. hydrogen chloride 1 vol. nitrogen + 3 vols. hydrogen \rightarrow 2 vols. ammonia.

In place of the term *volume* one may substitute any known measure of volume such as the cubic foot, cubic inch, or liter.

The above information, together with other facts of a similar nature, led to the Law of Combining Gas Volumes which states that chemical reactions between gases take place in such a manner that the ratio of the volumes involved is expressed by small whole numbers.

Avogadro's Law. The Law of Combining Gas Volumes which Gay-Lussac formulated was known to supply valuable information concerning the nature of matter but no one seemed to know what to do with it. In 1811, Avogadro, an Italian physicist, suggested the theory that equal volumes of all gases, at the same temperature and pressure, contain equal numbers of molecules. This was called Avogadro's Hypothesis but later evidence has so firmly fixed the truth of the statement that it is now known as a law.

Avogadro did not succeed in convincing most scientists of his day that his ideas were correct since his method of reasoning out his hypothesis is not at all obvious. Many workers still maintain that he merely made a lucky guess and this may be entirely true. Until 1858 there were no recognized differences between atoms and molecules, and the two terms were used interchangeably. It is not at all surprising, therefore, to find the interpretations of experimental results during that time to be somewhat confused. It was at this time, almost a half century after Avogadro proposed his theory, that an Italian chemist, named Cannizzaro, re-examined the evidence for atoms and molecules, and, by the help of Avogadro's hypothesis, explained many of the observed but confusing facts.

The main point of Cannizzaro's contribution centered around the difference between atoms and molecules. Thus, he said that molecules may contain several atoms and this fact may be used to account for the law of combining volumes. As an example of his reasoning let us consider the union of hydrogen with chlorine which was mentioned earlier. One vol-

ume of hydrogen combines with one volume of chlorine to form two volumes of hydrogen chloride. According to the ideas of Cannizzaro this may be explained as follows:

- 1. Equal volumes of all gases at the same temperature and pressure contain equal numbers of molecules, therefore, the number of molecules of hydrogen chloride formed must be twice the number of molecules of hydrogen and also twice the number of molecules of chlorine which united.
- 2. Each molecule of hydrogen chloride must contain at least one atom of chlorine and one atom of hydrogen. Then it must be that the number of atoms of hydrogen which united with chlorine is twice the number of molecules of hydrogen. In a like manner the number of atoms of chlorine, which united with hydrogen, is twice the number of molecules of chlorine.
- 3. Each molecule of hydrogen and each molecule of chlorine must be made up of at least two atoms of the element. For the sake of simplicity and in keeping with other evidence, we shall accept the value as two rather than four or some other multiple of two.

The reasonable character of the argument which is presented above may be realized better by means of diagrams. Of course, it is impossible to see the molecules because of their extremely small size and it is impossible to represent the actual number present in any volume of gas because this number is so large, but it is possible to imagine a very small volume of a gas enlarged to usable dimensions. Suppose that we assume the truth of Avogadro's Law and represent equal volumes of hydrogen and of chlorine containing a convenient number of molecules. The reaction may then be pictured according to the following scheme:

1 vol. hydrogen + 1 vol. chlorine \rightarrow 2 vols. hydrogen chloride



Fig. 20. One Volume of Hydrogen Reacts with One Volume of Chlorine

It does not matter whether the chosen volume contains three molecules or three million molecules since the same relative numbers would be involved in either case. We may conclude that if the hydrogen molecule and the chlorine molecule each actually do contain two atoms then the volumes of the gases involved in their union would be expected to be as found by experiment. Thus, we say that these two elements have *diatomic* molecules.

We may now return to the original question concerning the union of oxygen with hydrogen to form water. It will be recalled that experimentally one volume of oxygen unites with two volumes of hydrogen to form two volumes of water vapor. Again, since equal volumes of gases at the same temperature and pressure contain equal numbers of molecules, we are led to the following conclusions:

- 1. The number of molecules of hydrogen used is the same as the number of molecules of water which are formed. By the same reasoning it is twice the number of molecules of oxygen used.
- 2. Each molecule of water must contain at least one atom of oxygen and therefore the number of atoms of oxygen must be twice the number of molecules of oxygen.
- 3. Each molecule of oxygen must contain at least two atoms of the element. Again it appears best to let this stand as two rather than a multiple of two.

Again we may draw pictures to represent such a change.

2 vols. hydrogen + 1 vol. oxygen \rightarrow 2 vols. water vapor



Fig. 21. Two Volumes of Hydrogen React with One Volume of Oxygen

It appears that in this case, too, the volumes of gas are found experimentally to be the same as would be predicted if the molecules were exactly as shown. This seems sufficient argument to justify the statement that oxygen molecules are also diatomic.

One more example will be given. It has been stated that three volumes of hydrogen will combine with one volume of nitrogen to form two volumes of ammonia. This may be represented by the same scheme. From this it is evident that the nitrogen molecule must also be diatomic.

3 vols. hydrogen + 1 vol. nitrogen \rightarrow 2 vols. ammonia

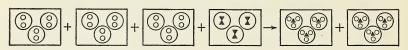


Fig. 22. Three Volumes of Hydrogen React with One Volume of Nitrogen

Here, also, the explanation and the facts seem to fit.

There is one point concerning the above discussion which frequently causes confusion but which a slight consideration will entirely clear up. So often a person will ask how it is possible for a molecule which contains four atoms to occupy the same space as a molecule which contains only two atoms. The actual size of the molecule does not govern the volume of the gas since the space between the molecules is many hundred times greater than the real volume of the molecules. A small increase in the size of the molecules will have almost no effect upon the volume of the gas as a whole. With this in mind one may see why it is possible for the original four volumes of hydrogen plus nitrogen to shrink to two volumes of ammonia.

The reasoning as outlined appears to explain the law of combining volumes and at the same time it accounts for the law of definite composition. If the average weight of all hydrogen atoms is the same wherever they may be found and if the same is true for all oxygen atoms then it becomes obvious that molecules of water will have the same average composition wherever they are found.

Symbols and Formulas. It is rather inconvenient always to write out the names of the elements and the composition of compounds in words. Abbreviations for the elements have

therefore been agreed upon and these are called chemical symbols. Thus the *symbol* for oxygen is O, for hydrogen is H, for nitrogen is N, and for chlorine is Cl. The symbols for the other elements may be obtained from the table on page 86. Since it has been shown that the above elements contain two atoms to the molecule we must write the abbreviations for them as O₂, H₂, Cl₂, and N₂ if we wish to represent the actual molecules of the free gas.

In a similar manner we may express the composition of a compound which contains more than one element. We have seen that a molecule of hydrogen chloride contains one atom each of hydrogen and chlorine so this may be written as HCl. In a like manner we may designate water as H₂O and ammonia as NH₃. This grouping of the symbols so as to show the number of each kind of atom contained in the molecule is called a chemical formula.

Atomic Weights. We have accounted for the volume relations encountered when hydrogen and oxygen unite to form water. It now remains to make use of the weight relationships in the same change. It has been noted that by weight 2.016 parts of hydrogen unite with 16 parts of oxygen. In the light of what has gone before we are able to arrive at a comparison between the weights of the atoms of these two elements. Since two volumes of hydrogen unite with one volume of oxygen we have shown that this corresponds to the union of two molecules of hydrogen and one molecule of oxygen. We see at once that two molecules of hydrogen must have a relative weight of 2.016 compared with one molecule of oxygen with a weight of 16. From the viewpoint of atoms we may use the same relative figures. The molecule of water is H2O and thus two atoms of hydrogen must weigh 2.016 weight units if the atom of oxygen is considered as weighing 16 units. One atom of hydrogen may then be considered as weighing 1.008 units. Of course, it is impossible to weigh an individual atom and if we could do so there is no suitable unit for expressing such a small value, but we can express the weights of the atoms with relation to each other. Very careful experimental work and

INTERNATIONAL ATOMIC WEIGHTS

1939

	Sym- bol	Atom: Numb	ic Atomic er Weight		Sym- bol I	Atomi Numb	ic Atomic er Weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Ве	4	9.02	Osmium	Os	76	190.2
Bismuth	$_{ m Bi}$	83	209.00	Oxygen	0	8	16.0000
Boron	В	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.57	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	\mathbf{F}	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.06
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Но	67	163.5	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0081	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	Ι	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.84	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	175.0	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	$_{\mathrm{Hg}}$	80	200.61	Zirconium	Zr	40	91.22

thousands of hours of study and research have carried this comparison to all the elements for our use. In order that these relative weights may be given in usable form it has been necessary to decide upon one element as a standard. Since oxygen is so abundant and combines easily with so many other elements it is a convenient one to use, and a value of 16 for the weight of the oxygen atom permits a value greater than 1 for the lightest atom which is hydrogen. By international agreement the relative weights of the atoms of all the elements are listed with reference to the oxygen atom as exactly 16. This international table of atomic weights is given on page 86.

Molecular Weights. After having determined the relative atomic weights by suitable experimental methods, it would appear possible to find the relative weights of molecules by simply adding up the total weight of all the atoms in the molecule. This method is entirely satisfactory if we first know how big the molecule is, that is, what its weight is in comparison with the oxygen atom. There are independent methods of finding the molecular weights of compounds, and one of these will be discussed at this time. If the oxygen atom as 16 is taken as the standard for comparison, then the oxygen molecule which contains two atoms must be twice as heavy and weigh 32 units. Now any unit may be used for weighing quantities of substances but in all scientific work the unit is the gram. It does not mean that the oxygen molecule weighs 32 grams but we may easily obtain enough oxygen to weigh 32 grams. This then will be as many grams of oxygen as there are units in its molecular weight but the actual number of molecules will be beyond counting. Such an amount of oxygen is termed the gram-molecular weight. If we measure the volume of oxygen so weighed it is found to be 22.4 liters when the temperature is 0° C. and the pressure is 760 mm. (Standard Conditions). Since 32 grams of oxygen is termed the gram-molecular weight it naturally follows that we should term 22.4 liters as the gram-molecular volume.

Suppose now that for comparison we measure out a like volume of any other gas at standard conditions. Since equal

volumes will contain equal numbers of molecules it follows that 22.4 liters of any gas should contain the same number of molecules as this voume of oxygen. Whatever this volume of any other gas weighs will then be its gram-molecular weight. Because of this it is possible to obtain the molecular weight of any substance which may be converted to a gas. There are other methods for getting this value but this gives us enough of a picture of the chemist's method for the time being.

Avogadro's Number. One may wonder how many molecules there are in a gram-molecular weight of a gas, but the task of counting all of them would be impossible even if they could be seen. A number of investigators have devised methods which enable one to get some idea of this number by physical measurements, and it is interesting that all these methods give values which so much agree among themselves that if we could count molecules we would probably find them near these estimates. This number, called Avogadro's Number, is 6.062×10^{23} and is accurate to \pm .001. That is to say, the figure may be 6.061 or 6.063 but the methods used for getting the value do not permit of a decision. Just how big this number is no one knows since it is beyond the power of human comprehension. If it were possible to count the molecules and one could put 100,000,000 people (approximately the number in the U.S. who can count) to work at the job, each counting one molecule per second for twenty-four hours each day, it would require almost 200,000,000 years for them to count this number. Since the gram-molecular volume of any gas at standard conditions is 22.4 liters (slightly less than six gallons) it is obvious that even very small volumes of a gas contain enormously large numbers of molecules.

Another illustration has been given by someone. If an ordinary drinking glass of liquid water is poured into the sea, and in the course of time this becomes uniformly distributed through the sea, the rivers, and all the water in and around the earth; and then if a similar glass of water is taken from any river or sea, this will contain about 1000 molecules that were in the original glass of water.

Formulas from Percentage Composition. By the use of methods which have been developed by hundreds of scientists through the years, it is usually possible to determine the presence of the various constituent elements in a compound (qualitative analysis) and to determine their actual amounts (quantitative analysis). From these results it is possible to express the percentage composition of the substance. From such analytical methods it has been observed that water contains 11.19 percent of hydrogen and 88.81 percent of oxygen. This means that 100 parts by weight of water are made up of 11.19 parts by weight of hydrogen and 88.81 parts by weight of oxygen. The question then arises as to how many atoms of each element are present. Since we know the relative weights of each kind of atom and the relative amounts of each present in water it is possible to get the relative number of each kind of atom. Each hydrogen atom has the relative weight of 1.008 and thus it follows that 11.19 parts by weight of hydrogen will contain 11.19 ÷ 1.008 or 11.10 atomic weights of hydrogen. In a similar manner we may see that 88.81 parts by weight of oxygen will contain 88.81 ÷ 16 or 5.55 atomic weights of oxygen. Of course, it is impossible for a fraction of an atom to combine, but the relative numbers of hydrogen and oxygen atoms present in the water molecule are given by these figures. From this information we may write the formula of water as H_{11.10}O_{5.55} but we prefer that the formula express the number of each kind of atom in a single molecule. In all scientific work it is desirable to use the simplest expressions possible and thus we prefer to simplify the formula which was written. It is obvious in this case that the number of hydrogen atoms is twice the number of oxygen atoms and so the simplest formula is H2O. To arrive at this simplest formula in any case we have only to divide each of the subscript numbers by the smallest one.

Another example will make the method more clear. A compound, upon analysis, is found to contain 75 percent of carbon and 25 percent of hydrogen. From the table one finds the atomic weight of carbon to be 12. Thus in 100 parts by weight

of the substance there are $75 \div 12$ or 6.25 atomic weights of carbon and there are $25 \div 1.008$ or almost exactly 25 atomic weights of hydrogen. The formula could be written as $C_{6.25}H_{25}$ but it is more simple to divide each of these numbers by the smaller one and use the whole numbers so obtained as the subscripts. Thus $6.25 \div 6.25$ is 1 and $25 \div 6.25$ is 4, and the formula may be written as CH_4 . Due to unavoidable errors in analyses, the results never check exactly to every figure. Thus we get results such as the one above in which we simply must round off the number to 25 instead of a number just a fraction smaller than that.

Formula Weights. Formulas and atomic weights have been determined by experiment and from this knowledge it is possible to calculate the weight expressed by a formula. In the case of H_2O , for instance, the formula implies two atomic weights of hydrogen and one atomic weight of oxygen. The formula weight then is (2×1.008) plus 16 or 18.016 and this is the same as the molecular weight. If the formula for any substance is known it is possible so to calculate the formula weight at once.

Combining Number or Valence. In dealing with water, we see the formula is H₂O which means that one oxygen atom is able to combine chemically with two hydrogen atoms. At the present time we shall make no statements as to why this may be, but we shall accept it as an experimental fact. On the other hand we have seen the reason for assuming that one atom of chlorine is able to combine with only one hydrogen atom to form hydrogen chloride, which we write as HCl. Also we have explained evidence for the existence of ammonia as NH₃, and have seen an example concerning a substance found in natural gas in which one carbon atom is combined with four hydrogen atoms as CH₄. Now there are no cases known in which one hydrogen atom is combined with more than one atom of any other element and so it is used as a standard for comparison. Those elements whose atoms can combine with only one hydrogen atom are said to have a combining number of one, while the others are designated in a similar fashion.

Thus in the above examples the combining number of chlorine is one, of oxygen is two, of nitrogen is three, and of carbon is four. All of the elements may be classed in this fashion, either by direct comparison with hydrogen or by indirect comparison through some other element. For instance, the element iron, symbol Fe, does not combine with hydrogen, but its union with chlorine to form FeCl₃ places its combining number as three. Instead of using the term *combining number* it is customary to designate the same thing by the term *valence* which means "combining capacity." The explanation which is used to account for the different combining numbers belongs to another chapter.

Combining Weights. We have shown that oxygen has a combining number of two. We cannot say that one half of an atom of oxygen will combine with an atom of hydrogen because the oxygen atom cannot be split. We can say, however, that one half of a gram atomic weight of oxygen will combine with a gram atomic weight of hydrogen. That is, 8 grams of oxygen is chemically equivalent to 1.008 grams of hydrogen. Since the atom of hydrogen is taken as the standard of combining number it is also taken as the standard of combining weights. That weight of any element which will combine with 1.008 grams of hydrogen is called its combining weight. Since some elements will not combine with hydrogen it is necessary to get at their combining weights by reacting them with oxygen and use 8 grams of that element as the standard.

On this basis we are able to say that the combining number of chlorine is the same as the atomic weight, 35.46. The combining weight of iron in FeCl₃ is one third of the atomic weight or $\frac{1}{3}$ of 55.84 which is 18.61. Then if 18.61 grams of iron is chemically equivalent to 1.008 grams of hydrogen and, also, 8 grams of oxygen is equivalent to 1.008 grams of hydrogen we should be able to say that 18.61 grams of iron is chemically equivalent to 8 grams of oxygen. This is true and we find just that relation between their weights in Fe₂O₃.

CHEMICAL EQUATIONS

Earlier in this chapter we considered the evidence for writing the molecule of oxygen as O2 and the molecule of hydrogen as H₂. In Figure 21 the union of two hydrogen molecules with one oxygen molecule was represented in picture form. We also have discussed atomic weights, molecular weights, and the method of arriving at a chemical formula. By this time it should be apparent to us that chemical changes take place in a definite manner. Because of this we are able to make exact statements about the numbers of molecules which react, the weights of each reacting substance and product, and the volumes of any gases which enter the reaction or are produced by it. To tell all of this in words requires several lines of writing and before we can discuss many different chemical changes we will become thoroughly bored. To get away from such lengthy discussions, the chemist has a system whereby he makes use of chemical formulas arranged in the form of a chemical equation.

In order to make the chemical equation usable it has become necessary to agree upon certain points of use. We must use the symbol for an element to represent an atomic weight of that element. Thus when we write the symbol, O, for oxygen we mean 16 parts by weight of oxygen. If we write the formula for the oxygen molecule, O₂, we mean 32 parts by weight of oxygen. In the reaction of oxygen with hydrogen to form water we may recall that two molecules of hydrogen react with one molecule of oxygen to form two molecules of water. The two molecules of hydrogen are written as 2 H₂ and the two molecules of water are written as 2 H₂O. Let us list the available information in equation forms.

² volumes of hydrogen + 1 volume of oxygen \rightarrow 2 volumes of water vapor

² molecules of hydrogen + 1 molecule of oxygen \rightarrow 2 molecules of water

² molecular weights of hydrogen + 1 molecular weight of oxygen \rightarrow 2 molecular weights of water

 $2(1.008 \times 2)$ grams hydrogen + 2 × 16 grams oxygen $\rightarrow 2(1.008 \times 2 + 16)$ grams water.

Now this may be expressed as a simple chemical equation.

$$2 H_2 + O_2 \rightarrow 2 H_2O$$

Everything which is expressed in the four statements above the equation is also stated (by agreement) in the equation. At first glance the equation shows the number of molecules of each substance concerned but it also shows the number of atoms of each element present. Since it is agreed that an atomic weight of an element is represented by each symbol we may at once obtain the relative weights of each substance by consulting the table of atomic weights. For each formula weight of a gas we also have a definite volume (22.4 liters). Thus in a short chemical equation we may express quite a bit of information.

It is not at all difficult to write chemical equations if we know enough about the chemical changes to which the equations apply. It is true, however, that we must know all of the required information before we can represent a change in this way. We must know the formulas for the reacting substances as well as for the products. We also must know the relative amounts of each which take part in the reaction. All of this must be determined, at some time, by experiment but when it has once been determined and recorded we are at liberty to use it without further experimentation. For the usual beginner in chemistry the writing of equations seems quite complicated and it appears necessary to memorize them. This is far from the truth. It is entirely unnecessary to memorize any equation and furthermore it is undesirable to do so. The writing of equations comes best after a great amount of practice and then it is simple indeed. Unless the use of the equations is important enough to merit the practice necessary then nothing is to be gained by memorizing them. In the pages which are to follow we shall make use of equations at every possible opportunity. It will be helpful if the reader will take the time to observe each equation carefully.

Let us review some of the chemistry of oxygen and write chemical equations for the changes which take place. Oxygen may be prepared from mercuric oxide by heating.

It may be prepared by heating barium dioxide.

Oxygen may also be prepared from potassium chlorate by heating.

Oxygen will combine directly with all of the metals except a few such as gold and platinum which we call the noble metals. The union of oxygen with some metals takes place much more rapidly than with others. If magnesium is heated in a flame in the air it burns with a brilliant white light.

If small strips of iron such as steel wool are heated to a bright red-heat and then quickly placed in oxygen the iron will burn with a shower of sparks.

The relatively inactive metal, copper, which shows little signs of reacting with oxygen in the air, will combine rapidly with oxygen if it is heated red-hot.

Some of the nonmetals will react with oxygen just as fast as do the metals. Most of us are familiar with the burning of sulfur which takes place readily. If the burning sulfur is placed in pure oxygen the burning occurs with a brilliant blue flame.

$$\begin{array}{ccc} \text{Sulfur} & + & \text{oxygen} & \rightarrow & \text{sulfur dioxide} \\ S & + & O_2 & \rightarrow & SO_2 \end{array}$$

The burning of carbon is a common experience.

$$\begin{array}{ccc} \text{Carbon} & + & \text{oxygen} & \rightarrow & \text{carbon dioxide} \\ \text{C} & + & \text{O}_2 & \rightarrow & \text{CO}_2 \end{array}$$

Many compounds react with oxygen. The chief component of natural gas is called methane and it has the formula CH₄. If ignited in the presence of air or oxygen it burns.

Methane
$$+$$
 oxygen \rightarrow carbon dioxide $+$ water CH_4 $+$ 2 O_2 \rightarrow CO_2 $+$ 2 H_2O

One of the components of manufactured gas used in some cities is carbon monoxide. With oxygen or air it will burn.

Gasoline is a mixture of a number of compounds which contain carbon and hydrogen. We may assume it to contain octane which has the formula C₈H₁₈. It, too, burns with air or oxygen.

Octane + oxygen
$$\rightarrow$$
 carbon dioxide + water 2 C_8H_{18} + 25 O_2 \rightarrow 16 CO_2 + 18 H_2O

Paper is largely made up of cellulose which has the formula $C_6H_{10}O_5$ and we may write an equation to represent its burning.

Cellulose + oxygen
$$\rightarrow$$
 carbon dioxide + water $C_6H_{10}O_5$ + 6 O_2 \rightarrow 6 CO_2 + 5 H_2O

Oxygen will unite with certain mineral substances if they are heated in the air. The ore, zinc sulfide, from which zinc is prepared is thus treated.

Zinc sulfide
$$+$$
 oxygen \rightarrow zinc oxide $+$ sulfur dioxide 2 ZnS $+$ 3 O $_2$ \rightarrow 2 ZnO $+$ 2 SO $_2$

These are only a few of the reactions in which oxygen takes part but they may serve to give some idea of the use of equations.

SUMMARY

Chemical reactions between gases take place in such a way that the volumes of the reacting gases are related as small whole numbers.

Equal volumes of all gases, at the same temperature and

pressure, contain an equal number of molecules.

Molecules are made up of atoms. Each molecule of a substance contains at least one atom of each element of which it is composed. The relationship between the volumes of reacting gases can be explained on this basis.

The ordinary gaseous elements, oxygen, hydrogen, chlorine, and nitrogen have diatomic molecules and their molecular

formulas are written as O2, H2, Cl2, and N2.

The relative weights of the atoms compared to the oxygen atom as having a weight of 16 are called the atomic weights. The sum of the atomic weights of all the atoms expressed in a formula is called the formula weight or molecular weight. The molecular weight expressed in grams is called the grammolecular weight. This amount contains 6.06×10^{23} molecules.

Formulas for compounds are obtained from the percentage composition as determined by analyses. The formula merely expresses the number of each kind of atom present in the molecule.

Some elements have a greater combining capacity than do others. The combining capacity of hydrogen is taken as a standard and that of other elements are compared to it. The resulting whole numbers are called combining numbers.

That weight of any element which will combine with 1.008 grams of hydrogen or with 8 grams of oxygen is called its

combining weight.

REVIEW QUESTIONS

- 1. State Gay-Lussac's law of combining volumes and give illustrations.
- 2. What contribution was made by Avogadro to the explanation of Gay-Lussac's law?
- 3. What is the difference between the atom of hydrogen and the molecule of hydrogen?
- 4. Give evidence for the diatomic nature of the chlorine molecules.
- 5. By what reasoning do we assume that nitrogen molecules are best expressed as N₂?
 - 6. What is meant by the term, gram-molecular volume?
- 7. A liter of a gas at standard conditions weighs 1.429 grams. What is its molecular weight?
- 8. What weight of an element is represented by its symbol? What weight of a compound is represented by its formula?
 - 9. What is expressed by the formula of a substance?
- 10. A compound was analyzed and found to contain 52.17 percent carbon, 13.13 percent hydrogen, and 34.79 percent oxygen. Calculate its simplest formula.
- 11. For what reasons is oxygen used as the standard of atomic weights?
 - 12. What is Avogadro's number? What does it represent?
- 13. Calculate the formula weight of each of the following compounds: CH₄ (methane); NaCl (soduim chloride); CuSO₄ (copper sulfate); BaO₂ (barium dioxide); KClO₃ (potassium chlorate).
- 14. The formula of hydrogen sulfide is H₂S. What is the combining number of S?
- 15. The formula of aluminum chloride is AlCl₃. What is the combining number of Al?
- 16. What is the combining number of oxygen in H₂O? In Al₂O₃?
- 17. In an experiment in which tin was burned in oxygen it was found that 2.97 grams of tin (Sn) combined with 0.8 gram of oxygen. What is the combining weight of tin?
- 18. The combining weight of tin as determined in No. 17 will combine with what weight of chlorine?

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WATER: ITS COMPOSITION, CONTINUED

HYDROGEN

The element, hydrogen, which is released at the negative electrode during the electrolysis of water is of considerable importance. The free element is present in the atmosphere in minute traces only but its compounds are relatively abundant in the earth's crust. The percentage of hydrogen, by weight, in the things about us is quite small because the hydrogen atoms are so very light, but it is probable that no element other than oxygen furnishes more atoms for the crust of the earth than does hydrogen. It is found in combination with oxygen in water where it furnishes about one ninth of the total weight. In combination with carbon it is found in natural gas, in petroleum, and in products such as gasoline, kerosene, and lubricating oils which are prepared from petroleum. A considerable amount of combined hydrogen is found also in coal. Together with carbon and oxygen, hydrogen is present in the compounds which make up plant and animal products such as starch, sugar, cellulose, fats, oils, perfumes, and flavors. In fact it seems that hydrogen is almost as important to living matter as is carbon.

The Union of Hydrogen with Oxygen. One of the most characteristic properties of hydrogen is its violent union with oxygen to form water when the two are mixed in the presence of a flame or a spark. We have written the chemical equation for this union but nothing has been said about the amount of heat evolved. For every molecule of water formed from these elements there is a definite quantity of heat released and the equation may be written to include this.

By this we mean that when two gram-molecular weights of hydrogen combine with one gram-molecular weight of oxygen it forms two gram-molecular weights of water and releases 136,540 calories of heat. We may write this another way. $2(1.008 \times 2)$ grams hydrogen $+ 2 \times 16$ grams oxygen $\rightarrow 2(2 \times 1.008 + 16)$ grams water and liberates 136,540 calories of heat.

This unit of heat, called the calorie, is the amount of heat which is required to heat a gram of water one degree centigrade. As water is heated from 0° C. to 100° C., it is found that the amount of heat required for each degree of temperature change is not exactly the same. The average over this range of temperature is the same as that required to heat the water from 15° C. to 16° C. and so this value is taken as the standard. It may be seen that the heat produced during the formation of two gram-molecular weights of water (slightly more than 36 grams) is enough to raise the temperature of 136,540 grams of water (nearly 40 gallons) one degree C.

Catalysis Again. It has been shown by experiment that a mixture of hydrogen and oxygen, when perfectly dry, will not be ignited by an electric spark. The presence of a mere trace of moisture, however, enables the spark to start the combustion which takes place explosively. Just what the effect of this trace of moisture is we do not know, and it is hard to find the answer, but we do know that it is typical of the action of catalytic agents in general. Many chemical changes take place slowly, if at all, until some specific foreign material is added to the reacting mixture and then the reaction may proceed rapidly (see the preparation of oxygen from potassium chlorate). It frequently happens that this foreign material is unchanged and may be fully recovered but its presence somehow speeds up the chemical reaction enormously. We may conclude that a trace of water acts as a catalyst for the union of hydrogen and oxygen.

Industrial Use of the Hydrogen Flame. The enormous amount of heat which is evolved when hydrogen combines with oxygen is utilized in the welding of metals. For this pur-

pose a special burner known as the oxy-hydrogen blow torch is used. With this instrument a stream of hydrogen is burned in a stream of oxygen and the heat evolved is sufficient to melt

most of the metals. There are certain disadvantages which go with the use of these two gases and greatest is the danger of explosions. A tank of hydrogen is a potential source of an explosion if the released gas is improperly handled. Most of the flamewelding of metals is done by burning acetylene with oxygen. Acetylene contains a large percentage of carbon and with certain metals some of this carbon reacts, or is absorbed by the metal, and the resulting weld is less useful. For such metals the use of the oxy-hydrogen flame is quite desirable. This is particularly true in the case of some of the newer alloys (mixtures of metals with special uses).

Atomic Hydrogen Flame. About 1926, Irving Langmuir made a remarkable discovery concerning hydrogen. When hydrogen gas is passed through an electric arc it absorbs a large amount of energy which is given up at once after the gas

O₂ H₂

Fig. 23. The Oxyhydrogen Blowpipe

leaves the arc. This was explained by Langmuir as involving the splitting of hydrogen molecules to give hydrogen atoms under the influence of the energy in the electric arc.

$$H_2$$
 + electrical energy \rightarrow H + H

As soon as the atoms of hydrogen get away from the electric arc they recombine and give up their extra energy in the form of heat. This latter change may be written in terms of calories.

$$H + H \rightarrow H_2 + 90,000$$
 calories

A torch-like apparatus has been built which takes advantage of this absorption of energy and its subsequent release. By means of it a stream of hydrogen is sent through a hot electric arc and may be directed against a piece of metal which is to be welded. The large amount of heat which is absorbed from the arc is released at the metal, and in addition to this the hydro-

gen burns to get the metal still hotter. The total heat evolved is great enough to permit the attainment of temperatures as high as 5000° C. Extremely important welds where flaws must not be present are made by this process.

Hydrogen as a Chemical Reagent. Within recent years hydrogen has taken on added importance as an industrial chemical reagent. This has been due, in part, to its production at lower costs which has made it available to new industries. In addition to this there have been new uses discovered. A few of the industries which use large amounts of hydrogen are briefly described.

Hydrogenation of Fats. Certain naturally occurring oils such as cottonseed oil and cocoanut oil are liquids at room temperature and are not adapted to cooking purposes because we prefer to use solid fats for this. Now all of these oils contain a considerable amount of hydrogen in their molecules but they are able to combine with still more of this element under the proper conditions. After combining with additional hydrogen the resulting material is a solid at room temperature and is satisfactory for use in cooking. Thus if cottonseed oil is heated to 175° C. and treated with hydrogen under pressure, in the presence of specially powdered nickel as a catalyst, the union with hydrogen takes place. The resulting hot oil is filtered to remove the nickel and then is allowed to cool to a solid. We are acquainted with the product in the form of "Crisco," "Spry," and "Snowdrift." Some oils which are not suitable for eating are also "hydrogenated" in this manner for the manufacture of soap. In 1939 there were more than 410,000 tons of oil so treated. Each ton of oil requires 2000 or more cubic feet of hydrogen.

Synthetic Wood Alcohol. When carbon monoxide and hydrogen are passed together over a suitable catalyst they unite to form methyl alcohol. This substance is known as synthetic wood alcohol and is given the name methanol to prevent confusion with grain alcohol. The 1939 production of this synthetic product was 34,000,000 gallons and the rate of production in 1940 is still greater. More than five billion cubic feet of hydrogen was required for

the output of last year.

Synthetic Ammonia. We have already mentioned the importance of nitrogen compounds to fertilizers and explosives. The

greatest production of these nitrogen compounds from the nitrogen of the air is by way of the formation of ammonia. The ammonia may be changed to other substances as needed. Ammonia is produced by passing a mixture of hydrogen and nitrogen over a catalyst. The 1939 production of ammonia in the United States has been estimated as 260,000 tons. This would require 16 billion cubic feet of hydrogen.

Liquid Fuels from Coal. The production of liquid fuels from coal by the use of hydrogen has received considerable attention during the past few years. Coal is heated with hydrogen under pressure and some of the coal changes into liquid compounds which are much like gasoline. This process has been developed in Germany where motor fuel is in great demand and much more expensive than in the United States. Some experimental work has been done with this process in this country but so far it is of no importance to us. As long as we have large amounts of crude petroleum it will be hard to introduce other sources of liquid fuels.

Metals from Their Ores. The great reactivity of hydrogen with oxygen suggests another use for the gas. Many metals occur in the earth in the form of their oxides and to get the free metal the oxygen must be taken away. For some of these ores it is satisfactory to heat them with carbon which unites with the oxygen leaving the metal. There are cases of some metal oxides which will not yield the free metal with carbon and other cases where the metal content of the ore is too small to use carbon. Almost all oxide ores will give up their oxygen if they are heated with hydrogen.

Copper oxide may be converted to free copper quite easily by means of hydrogen.

$$CuO + H_2 \rightarrow Cu + H_2O$$

Iron oxide, which is the common ore of iron, is also converted to free iron.

$$\mathrm{Fe_2O_3}$$
 + 3 $\mathrm{H_2}$ \rightarrow 2 Fe + 3 $\mathrm{H_2O}$

As the supply of high grade ores of iron are exhausted it may become necessary to begin using ores which contain too little iron to handle in the usual way. The Bureau of Mines has already done considerable research looking toward the production of iron by means of hydrogen with low-grade ores. To make such a use possible will require the large scale production of cheap hydrogen.

The Production of Hydrogen. The production of pure hydrogen in sufficient quantities to meet all of the industrial uses has become important. An examination of the various methods will show the general processes which are used. As would be expected, it is necessary to start with a cheap, plentiful material if large amounts of the gas are to be prepared at as low a cost as possible. Since water is easily obtained and contains 11 percent of hydrogen it presents itself as the logical starting material for the production of commercial hydrogen.

The Electrolysis of Water. We have seen how the passage of an electric current through water liberates hydrogen. In this country the cost of electricity has been too great to permit much production by such a method.

Active Metals with Water. Certain metals are active enough chemically to take oxygen away from hydrogen if the conditions are properly adjusted. Among these are sodium, magnesium, aluminum, zinc, and iron. None of these can be supplied at a low cost except iron and this may be because such large quantities of it are obtained as scrap. If hot steam is passed over hot iron, in the form of very small pieces, the iron will combine with the oxygen in a part of the steam and will liberate some hydrogen. This will produce some iron oxide. It may be recalled that we have just considered the removal of oxygen from iron oxide by means of hydrogen. In the light of that information this removal of oxygen from water by means of iron seems queer. Let us write this chemical equation and consider the experimental facts of the case.

 $4 \text{ H}_2\text{O (steam)} + 3 \text{ Fe} \rightarrow 4 \text{ H}_2 + \text{Fe}_3\text{O}_4 \text{ (magnetic oxide of iron)}$

If the steam is sent through the apparatus which contains hot iron it will carry out any hydrogen as fast as it is formed. On the other hand, if we pass hydrogen over hot iron oxide it will react to produce some iron and steam. In this case the stream of hydrogen will carry away any steam as fast as it is formed. Here we have a chemical change that can take place in either direction depending upon the amount of reacting material present. If there

is a large amount of steam present it goes to form hydrogen; if a large amount of hydrogen is present it goes to form steam. Such a reaction which may be made to take place forwards or backwards is said to be *reversible*.

Suppose we think of a large container holding scraps of iron and filled with steam at a temperature near red-heat. In order that nothing may get in or out of our container we will close it tightly. After a time we may examine the contents of the container and find that a part of the steam has been changed and we have about one volume of hydrogen to six volumes of steam. If we repeat the experiment but use iron oxide and hydrogen and have the temperature the same as before we will find the same relative amounts of steam and hydrogen as the first time. We explain this peculiar behavior by saying that both changes take place at the same time but there is a condition where they take place at the same rate. At this particular temperature this occurs when the amount of steam is six times the amount of hydrogen (by volume). If the temperature is raised, the amount of steam present will become less and less until at 1500° C. the steam and hydrogen volumes will be equal. The condition of two chemical reactions taking place in opposite directions at equal rates is called equilibrium. We represent such an equilibrium by combining the equations for the two reactions.

 $4 \text{ H}_2\text{O} \text{ (steam)} + 3 \text{ Fe} \Leftrightarrow 4 \text{ H}_2 + \text{Fe}_3\text{O}_4 \text{ (magnetic oxide of iron)}$

By adding an excess of steam we get hydrogen or by adding an excess of hydrogen we could change the magnetic oxide of iron into iron.

Carbon with Water. The most widely used method for the production of hydrogen utilizes the reaction between steam and carbon at 1000° C. A bed of coke or anthracite coal is burned with air until it becomes white hot. The air supply is shut off and superheated steam is forced through the hot material. The reaction which takes place consumes energy in the form of heat and the bed of hot carbon is rapidly cooled.

 H_2O (steam) + C + 31,400 calories \rightarrow H_2 + CO (carbon monoxide)

It soon becomes necessary to turn off the steam and again let in air in order to reheat the carbon to the required temperature.

$$C + O_2 \rightarrow CO_2 + 94,400$$
 calories

This process may be controlled so that the collected gas contains only hydrogen, carbon monoxide, and carbon dioxide. These two oxides of carbon may be changed into liquids quite easily and thus removed, or the carbon monoxide may be oxidized by steam in the presence of a catalyst. This catalyst is a mixture of the oxides of iron, chromium, and thorium.

$$\mathrm{CO}\,+\,\mathrm{H_2O}\rightarrow\mathrm{CO_2}\,+\,\mathrm{H_2}$$

The hydrogen in the gas remains unchanged and the carbon dioxide may be dissolved if bubbled under pressure into water. This process supplies hydrogen both easily and cheaply.

Other Sources of Hydrogen. Compounds other than water may be used for the production of hydrogen though as a rule their cost prevents extensive application unless the hydrogen is a by-product or something else is produced at the same time and may be sold.

Metals with Acids. Hydrogen is contained in all of the substances which we commonly call acids. From some of these the hydrogen may be liberated by certain active metals. We have seen how iron may displace hydrogen from water at elevated temperatures. In like manner, iron will react with acids even at room temperature and cause the hydrogen of the acid to be set free. With hydrochloric (muriatic) acid iron reacts rapidly.

$$Fe + 2 HCl \rightarrow H_2 + FeCl_2$$
 (ferrous chloride)

Zinc and aluminum also displace hydrogen readily from this acid.

$$Zn + 2 HCl \rightarrow H_2 + ZnCl_2$$
 (zinc chloride)
2 Al + 6 HCl \rightarrow 3 H₂ + 2 AlCl₃ (aluminum chloride)

You may notice that in these equations it is necessary to use hydrogen atoms in multiples of two. This is due to the fact that there are two atoms in each hydrogen molecule.

If we use these same three metals with sulfuric acid we will again obtain hydrogen.

$$\begin{array}{lll} Fe & + \ H_2SO_4 & \rightarrow H_2 & + \ FeSO_4 \ (ferrous \ sulfate) \\ Zn & + \ H_2SO_4 & \rightarrow H_2 & + \ ZnSO_4 \ (zinc \ sulfate) \\ 2 \ Al & + \ 3 \ H_2SO_4 \rightarrow 3 \ H_2 \ + \ Al_2(SO_4)_3 \ (aluminum \ sulfate) \end{array}$$

For the production of small amounts of hydrogen any of these metals with either of these acids will give satisfactory results.

Metals with Bases. Such substances as caustic soda (sodium hydroxide) and caustic potash (potassium hydroxide) are called bases and they also contain hydrogen. These will react with several of the active metals and lose hydrogen.

Zn + 2 NaOH
$$\rightarrow$$
 H₂ + Na₂ZnO₂ (sodium zincate)
2 Al + 6 NaOH \rightarrow 3 H₂ + 2 Na₃AlO₃ (sodium aluminate)

A commercial product for cleaning household drains contains flakes of sodium hydroxide together with small bits of aluminum. When mixed with water these react to form hydrogen which stirs up the mass of accumulated dirt while the excess of sodium hydroxide dissolves the fat.

Petroleum Products. Petroleum products are compounds of carbon and hydrogen. If heated to a sufficiently high temperature these are all broken apart to give carbon and hydrogen. The carbon is in demand as a filler in the rubber of automobile tires and thus a considerable effort is being made to develop this process. It is already in use in the gas fields of Louisiana.

Heavy Hydrogen. References to heavy hydrogen are becoming so common in the daily press that it is necessary to refer to it here though an additional study will be made in a later chapter. Dr. Urey of Columbia University made the discovery that about one hydrogen atom out of every 5000 has an atomic weight of approximately 2. This heavy form of hydrogen has many of the chemical properties of hydrogen but as yet there are many experiments necessary before definite statements may be made concerning all of its chemical properties. It was discovered late in 1931 and since that time it has furnished the main interest for hundreds of research workers. It has been named deuterium and has been given the symbol D. The symbol for heavy water is D₂O and it is called deuterium oxide. We will discuss other elements having heavy and light forms and we shall say that they are isotopes. Thus deuterium is an isotope of hydrogen.

SUMMARY

Hydrogen is widely distributed in nature in the combined state. It occurs in water, in plant and animal tissues and

products, and in petroleum.

When hydrogen unites with oxygen it liberates large amounts of heat and it is thus used in the welding of metals. The atomic hydrogen flame gives a more intense heat due to the energy released as the atoms of hydrogen recombine to form molecules of hydrogen.

Hydrogen is used as a chemical reagent to produce solid fats from liquid vegetable oils by the process of hydrogenation. With carbon monoxide hydrogen will unite to form synthetic methyl alcohol. With nitrogen hydrogen may be made to react to form ammonia. Each of these processes requires a specific catalytic agent and specific conditions of temperature and pressure. The hydrogenation of certain low-grade coals has led to the formation of liquid fuels. Some ores of metals which are oxides may be changed to the free metal by the use of hydrogen.

Hydrogen may be produced from water by electrolysis, by the treatment of hot iron with steam, or by passing steam through beds of white-hot carbon. Certain metals such as zinc, iron, and aluminum will liberate hydrogen from acids such as hydrochloric and sulfuric. Zinc, aluminum, and a few other active metals will liberate hydrogen from bases. Petroleum products may be broken down by heat to give hydrogen

and carbon.

There are some chemical reactions which are reversible. These usually reach a state of equilibrium unless the products of one of the reactions are removed from the reacting vessel.

A part of the hydrogen in all substances has an atomic weight of approximately 2. This is known as deuterium or heavy hydrogen. It is an isotope of ordinary hydrogen.

REVIEW QUESTIONS

1. Would you expect the oxy-hydrogen flame to give a higher temperature than that produced by burning hydrogen with air alone? Explain.

2. Define the calorie. How many calories would be required

to heat a pound of water from 0° C. to 100° C.?

3. Define a catalyst. Give several examples of catalytic action.

4. In the production of hydrogen by the use of steam and iron is the iron a catalyst? Explain.

5. List the more important commercial uses of hydrogen.

Which of these require catalysts?

- 6. Why is hydrogen not used in the production of iron, copper, zinc, and other relatively cheap metals from their oxide ores?
- 7. Outline the methods for the production of hydrogen from water.
- 8. What is a reversible reaction? What do we mean by a chemical equilibrium?

9. Why is commercial hydrogen not produced from acids and bases?

10. List all of the methods of preparing hydrogen. Which are most used and why?

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WATER: LIQUIDS AND SOLIDS

Three States of Matter. So far, most of our discussion has concerned gases. But any gas may be converted to a liquid if the temperature is lowered enough. By increasing the pressure applied to a gas, the change to a liquid may usually be brought about at a higher temperature, except that for every gas there is a definite temperature above which no amount of pressure can bring about its liquefaction. This is called the critical temperature and it has been discussed under the behavior of gases. For water this temperature is 374° C. and the pressure required to keep water as a liquid at this temperature is 218 atmospheres. This is more than 3000 pounds per square inch. At 375° C. no pressure is large enough to keep water in the liquid form.

It is common experience that continued cooling of steam converts it to water and that further cooling soon converts it to a solid (ice) form. This is true also for any other pure substance, provided that the cooling is great enough. These three physical conditions: gas, liquid, and solid, in which a substance may exist are termed the *three states of matter*. In general, any substance may exist in any of the three states unless its decomposition prevents.

THE LIQUID STATE

Some of the differences between gases and liquids have already been mentioned. That the molecules of a gas are much farther apart than those of a liquid is shown by the compressibility of the two. Some gases may be compressed to a very small fraction of their original volume but liquids are usually

resistant to an increase in pressure. That the attraction between the molecules of a gas is less than the attraction between the molecules of a liquid is shown by the method used to confine each. A gas will diffuse outward from a container unless it is tightly closed upon all sides while a liquid is retained in a vessel enclosed on the bottom and sides but open at the top. This attraction between the molecules of a liquid is not sufficient to hold them rigid since a liquid flows downward at every opportunity as we see when a container springs a leak.

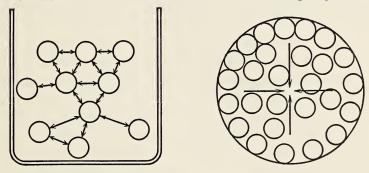


Fig. 24. Attraction between the Molecules of a Liquid

There is every reason to believe that the molecules of a liquid are moving just as are the molecules of a gas, but their movement is probably more of a zigzag nature and confined to a limited area rather than a continuous flow outward. Free motion for any distance is considerably hindered.

Surface Tension. If we try to imagine an enlarged view of the molecules in a liquid, we may arrive at a picture something like the accompanying diagram. There are two positions in which the molecules may find themselves. Either they will be in the surface of the liquid or they will be within the body of the liquid. If we represent the forces of attraction between the molecules by means of double-headed arrows we can see at once that those molecules within the body of the liquid are attracted by molecules on all sides while those in the surface are attracted by molecules to the side and downward only. It may readily be seen that such forces will tend to cause the surface molecules to be drawn closer together and toward

the center of the liquid. This effect is noticed in the spherical shape taken by drops of water. This extra attraction between the surface molecules is called the surface tension of the liquid. It acts to oppose any increase in the amount of surface.

Application of the Principle of Surface Tension. It is the surface tension of water which causes it to be drawn upward in the soil between the small particles of earth. This is usually referred to as capillary attraction but its cause rests in the surface tension of the water. The laundry industry has found that water alone does not rapidly wet the fiber of clothing since its surface tension prevents its penetration of the dry material. However, upon lowering the surface tension of the water by the addition of certain substances, a garment may be wetted much more thoroughly and rapidly. Certain "wetting agents" have been produced which seem to speed up laundry practice and these usually lower the surface tension of the water quite a bit. Considerable evidence has been put forward to show that certain antiseptics may be better because their solutions in water have a very low surface tension which permits their penetration into the germ cell.

Evaporation. Since the molecules of a liquid are usually like the molecules of the same substance in the gaseous form, except that they may be closer together and more restricted in their motions, we must expect them to behave toward heat in much the same manner. It seems only natural to suppose that some of the molecules of the liquid will be moving much more rapidly than others, and that, if we apply heat to the liquid, all of the molecules will move at a more rapid rate. This movement takes place in all directions, and a portion of the molecules must strike the upper surface of the liquid. Now we have seen that the surface of the liquid is made up of a layer of molecules which are drawn closer together and therefore it will be just a little difficult for a moving molecule to penetrate this surface. If, however, a few of the molecules are moving quite rapidly it may be possible for them to pierce this surface "skin." When once they are through the surface, the molecules may not have enough energy left to carry them

away. They may fall, or be drawn, back into the liquid. But, if they do get clear away, we say the liquid is *evaporating*. The faster the molecules within the liquid move the greater will be the possibility that some of them will get through the surface and thus evaporate. Since the speeds at which the molecules move depend upon the temperature of the liquid, it follows that an increase in the temperature should increase the evaporation.

Boiling Point. There is another effect which must be considered when we discuss evaporation. Above the liquid is the

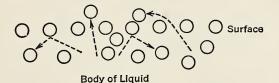


Fig. 25. Behavior of the Molecules at the Liquid Surface

atmosphere which is made up of rapidly moving molecules of air gases and unless the molecules of the liquid, which penetrate the surface, are moving rather rapidly they will be beaten back down into the liquid again by the bombardment of the molecules in the air. A few of the molecules from the liquid do possess enough speed to get away, and some evaporation takes place even at low temperatures. Even ice evaporates in freezing air. With an increase in temperature the number of liquid molecules which possess enough energy to get completely away against the atmospheric pressure is increased until a temperature is reached when all the molecules are in a condition to do so. As additional heat is added the liquid changes to a gas without change of temperature. It is at this temperature that free boiling takes place and it is termed the boiling point of the liquid. This temperature for any liquid will depend upon the atmospheric pressure, and, since this is less at high altitudes than at lower ones, it follows that water boils at lower temperatures if one carries out this process on a mountain of considerable height rather than at sea level.

Just as the molecules of a gas produce a pressure by their many impacts, so do the molecules of a liquid which break away from the surface. The greater the number which break away the greater this pressure will be and it is called the *vapor pressure* of the liquid. It follows from what has gone before that the boiling point of a liquid is the temperature at which the vapor pressure of the liquid is just equal to the atmospheric pressure.

Advantage is taken of the change in boiling point with pressure in many industries. If milk or sugar syrup is evaporated at atmospheric pressure, the temperature required is sufficient to destroy the substance. But, by evacuating the boiling pans, it is possible to remove the excess water at much lower temperatures. In the canning of food and in similar industries the pressure in the cooking vessel is increased by sealing the container as in a pressure cooker. This results in a much higher boiling point of the water and thus more rapid and thorough cooking or heating. These are equipped with safety valves to prevent the application of too much pressure which might easily blow up the cooker.

Heat of Vaporization. When a liquid is heated to its boiling point, its vapor pressure is equal to the atmospheric pressure. But, if the liquid is to evaporate, the volume which it occupies must be greatly increased. This expansion in volume requires that the air be pushed back and that the attraction between the molecules of the liquid be overcome. Both of these requirements can be met by the addition of energy to the molecules of the liquid. Expansion to the gaseous state cannot take place until the extra energy is supplied. Thus after a liquid is heated to its boiling point it is necessary that still more heat be supplied to bring about evaporation. This extra heat requirement is called the *heat of evaporation* and has the same numerical value as the *heat of condensation* which was mentioned earlier in connection with the liquefaction of gases. Every liquid requires a definite amount of heat for its evaporation, and for some this is quite high. For water this amounts to about 540 calories for each gram. This means that it takes

about 540 calories of heat to convert one gram of water at 100° C. to steam at 100° C. The temperature does not change, and the extra heat merely supplies the energy to separate the molecules and to push back the air.

Refrigeration. The heat of evaporation is important in mechanical refrigerators. A liquid which evaporates easily (volatile) is caused to evaporate by creating a partial vacuum over

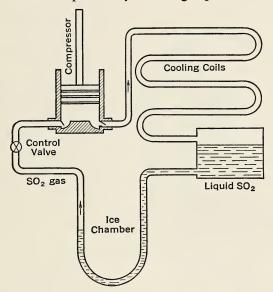


Fig. 26. Diagram of Refrigeration Machine

it. The evaporation which follows is made possible by means of heat which is supplied from the contents of the refrigerator. The gaseous material is condensed by means of pressure applied by a pump together with cooling by means of water or the air. The cooled liquid is then ready to be again evaporated within the box. A number of substances have been used for this purpose but the most successful ones are sulfur dioxide, ammonia, methyl chloride, and dichlorodifluoromethane (CF₂Cl₂) (Freon). All of these are gases at ordinary conditions but their critical temperatures are relatively high and thus they are easily liquefied at room temperature by pressure alone.

Air Conditioning. Aside from our clothing, there are two important factors which control the comfort of the body with regard to sensations of temperature. The first is, of course, the actual temperature of the surroundings and the second is the amount of moisture in the air. Our bodies have a natural cooling system which consists, in part, of the perspiration glands. The evaporation of the perspired moisture from our bodies re-

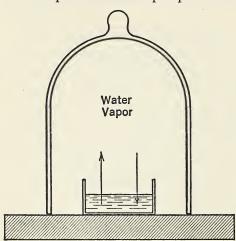


Fig. 27. Equilibrium between Water and Its Vapor

quires considerable heat and thus acts as a means for lowering the skin temperature. The more rapidly this evaporation takes place the cooler the surface of the body will be. Since the temperature of the body as a whole is quite constant, the rate of this evaporation cannot be controlled by the body but may be controlled by adjusting the water vapor in the air.

If we consider a closed vessel which is partially filled with water (Figure 27) we may get some idea of the influence of water vapor in the air upon the rate of evaporation. At first there may be very little water vapor in the air, and more molecules of water will leave the liquid to enter the air. After a time the number of water molecules in the air will become so great that just as many of them will strike the surface of the liquid as will leave this surface. Such a condition as this is one of complete saturation of the air. By raising the temperature of the water, still more molecules will evaporate, and, by cooling the vessel, some of the water vapor will condense. That is, water molecules will enter or leave the air until a new condition of equilibrium is set up. Now when the amount of water vapor in the air is low, in comparison with the amount which

is required for this equilibrium (saturation), evaporation of liquid water will take place rapidly. When the amount of water vapor in the air is relatively high, evaporation takes place slowly since the molecules of water from the air return to the liquid almost as fast as they leave the liquid.

It becomes obvious that in order to take advantage of the natural cooling of the body we must permit some evaporation of perspiration to take place, if this is at all possible. If the moisture content of the air is high, evaporation almost ceases and our bodies feel too warm, even though the actual temperature may be at the usual point of greatest comfort. This is what happens in hot moist climates. If the moisture content of the air is quite low, the rate of evaporation from our bodies becomes rapid and the cooling may be too great for comfort at the same temperature as was noted above. It is this which happens in our dry steam heated apartments in Northern cities. The modern plan of air conditioning seeks to adjust the moisture content of the air so that comfort results at a convenient temperature.

THE SOLID STATE

Heat of Fusion. If the temperature of water is lowered sufficiently, the molecular motion is slowed down until forces of molecular attraction are able to overcome much of the motion. This results in the sudden fixing of the positions occupied by the molecules so that any motion which they possess is a vibration about a point. This loss of motion is really a loss of kinetic energy, and, as such, this energy must appear in some other form. As is the case when a gas condenses to a liquid, the change from a liquid to a solid evolves heat which in this instance is called the *heat of solidification*.

To those who have observed crystals of ice, in the form of snow, it is apparent that the change from the liquid to the solid involves a regular arrangement of the molecules in varied and beautiful crystal patterns. When heat is applied to ice, and the solid melts, this orderly arrangement is destroyed and the forces of rigidity are overcome by the kinetic energy of the molecules. To bring this about requires the absorption of the same quantity of energy as is given up when a like amount of water changes to a solid. This heat which is required to change a solid to a liquid is called the *heat of fusion*. For water, this amount of heat is 79 calories per gram.

Melting and Freezing Point. For most substances the change from a liquid to a solid, or from a solid to a liquid, takes place at a definite temperature. This is termed the melting point of the solid or the freezing point of the liquid. While it is impossible to heat a solid above its melting point without melting it, yet a liquid may sometimes be cooled several degrees below its freezing point without solidifying it. The reason for this is quite simple. If the container is quite clean and free from rough surfaces, and if the liquid is not agitated, it is a little difficult for the molecules of the liquid to properly arrange themselves. However, if the liquid is stirred, or if a small bit of the solid is added, the molecules begin to align themselves at once with the evolution of the heat of solidification. This heat raises the temperature of the solid-liquid mixture up to the true freezing point where the temperature remains constant until all the liquid is converted to solid by further cooling. The melting of a solid involves the reverse of this process. First, the temperature of the solid is raised to the melting point and there the absorption of the heat of fusion begins. The regular order of arrangement of the molecules begins to disappear. Until all of the solid is changed to a liquid, the temperature does not change. Since the freezing point and the melting point of any particular substance are the same, it follows that a mixture of the solid and its liquid which have stood for some time will have this temperature. Thus, a water-ice mixture which has stood for some time in an insulated vessel will have a temperature of 0° C. In fact the melting and freezing points are defined as the temperature at which a solid and its liquid are in equilibrium.

The Structure of Solids. Some substances seem to become solids without any definite form and without any orderly ar-

rangement of the molecules. Such solids are termed *amorphous*, which means "without form," and these do not usually have a definite melting point. Glass is typical of such amorphous materials in that it softens and slowly melts over quite a range of temperature, but like many other such substances, glass is really a mixture of several things and is not a pure compound. Butter and lard are other examples.

The majority of pure substances exist as definite crystals in which molecular orderliness is quite apparent. The shapes which the crystals take probably depend upon the shapes of the molecules of which the substance is composed and upon the directions in which the attractive forces are acting. Thus water crystals are variations of the hexagonal, while salt crystals (common salt) are cubic or boxlike. In some instances the same substance may form crystals of different shapes if the conditions are changed and such substances are said to be polymorphous. This means that more than one stable arrangement of the molecules is possible, but, as a rule, one such arrangement is more stable than the others at any given temperature. Any other crystal form will slowly change to the most stable form though this may require months or even years. Water and sulfur are two outstanding examples of polymorphous substances. Objects of tin, used at ordinary temperature, tend to turn to a powder if kept for a long time at low temperatures. This, which is called "Tin Disease," is nothing more than a change in crystalline form. In those cases where an element is polymorphous, the various forms in which it exists are said to be *allotropic forms*. An example of this which is common to our experience is the existence of carbon both as diamond and as graphite.

Evidence for Molecular Motion in Solids. Probably the best evidence for the motion of the molecules in a solid is in the fact that most solids will evaporate. It is common knowledge that such solids as naphthalene (moth balls) and camphor will evaporate at room temperatures. It is the evaporation of these things which furnishes the molecules which reach our noses. Those who live in the colder climates frequently wit-

ness the slow removal of ice and snow by evaporation though the temperature remains below freezing.

Since molecular motion is necessary in order to account for this behavior of solids, it is generally accepted that such must exist. This is probably confined to a sort of vibration about a point rather than motion of any sort in a straight line. Such a conception gives continuity to our thoughts concerning solids, liquids, and gases, and does not seem at all unreasonable or improbable.

X-Rays and Crystal Structure. X-Rays are very short light waves which have something near the dimensions of molecules and atoms. By subjecting a crystal to a beam of x-rays and placing a photographic plate in the proper position it is possible to obtain a series of bright spots on the picture which are due to the reflections of the x-rays by the atoms or molecules within the crystal. A study of the results from many pictures enables one skilled in the work to construct a model showing the positions of the component parts of the crystal. While this new method of approach is quite important, its consideration is beyond our immediate scope.

SUMMARY

Many pure substances may exist as solids, liquids, or gases. These are known as the three states of matter. The particular state of a substance depends upon both the temperature and the pressure.

The molecules within a liquid are fairly close together and their motion is considerably restricted. Those within a solid are tied down to a particular locality by forces acting between them but some sort of vibratory motion of these molecules probably takes place.

The molecules at the surface of a liquid are drawn toward the center of the liquid. This force which is called surface tension operates so as to prevent the extension of the liquid

surface.

Those molecules of a liquid which move fast enough are able

to penetrate the liquid surface and gain access to the air, resulting in evaporation. When the pressure produced by the evaporating molecules equals the atmospheric pressure the liquid boils freely. The temperature at which this takes place is the boiling point of the liquid. The atmospheric pressure determines the boiling point of any liquid.

When a liquid changes to a gas it absorbs a large amount of energy, in the form of heat, which serves to separate the molecules and to push back the air. This is the heat of vaporization. The cooling produced in a mechanical refrigerator results from the heat absorbed by an evaporating liquid.

If the air over an evaporating liquid becomes saturated with the evaporated molecules a condition of equilibrium results and evaporation appears to stop. Moist air thus prevents normal evaporation from our bodies and we have a sensation of undue heat. Air conditioning attempts to control the moisture content of the air.

Heat is absorbed when a solid changes to a liquid. This is called the heat of fusion. This same quantity of heat is liberated when a liquid freezes. The melting point of a solid is the temperature at which the solid and its liquid will remain in contact without change. This is also the freezing point.

Pure solids have definite arrangements of the molecules in crystalline forms. When there are two or more forms of the same substance it is said to be polymorphous. The polymorphic forms of elements are said to be allotropic.

Crystal structure is studied by means of short x-rays which may be reflected by the individual molecules within the crystal.

REVIEW QUESTIONS

- 1. What changes must take place in order to convert ice into steam?
 - 2. What do we mean by kinetic energy?
- 3. Give evidence for the statement that the molecules of a gas are farther apart than are the molecules of a liquid.
- 4. What evidence is there for molecular motion within liquids and solids?

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5. Try to float a small dry needle on the surface of water. Why

is this possible?

6. Hold a piece of glass or a knife blade tightly against the inside of a tumbler partially filled with water. Note that the water crawls upward between the two surfaces above the level in the tumbler. Explain.

7. Define: heat of vaporization, heat of fusion. Why does the absorption of heat during these two processes not result in a

temperature rise?

8. Define boiling point. Why is this dependent upon the at-

mospheric pressure?

9. Would the temperature of water boiling in New York City be the same as that of water boiling in Denver? Why?

- 10. In a mechanical refrigerator, what process occurs within the coils inside the box? Within the coils on the outside of the box? Why do these outer coils get warm?
- 11. Why is it necessary to evaporate water within many steam heated rooms?
- 12. What term is applied to the different forms of elements such as carbon which are known in two or more crystal forms?
 - 13. Is it colder when you get out of a swimming pool on a

windy day? Explain.

14. Is it true that an egg boiled on Pikes Peak is not cooked? Explain.

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WATER: THE UNIVERSAL SOLVENT

Importance of Solutions. One of the most common properties of water is that it can dissolve and mix with certain other substances with which it comes in contact. The resulting mixture is called a solution. While it is true that all substances such as various rocks, metals, and living things are not noticeably soluble in water, it is remarkable that it probably has the ability to dissolve more things than does any other substance. The solutions formed in water are frequently of the utmost importance to both plants and animals. Our entire body operates as a water solution. As a noted medical man once remarked, "Each of us is chemically only a barrel of water and 87 cents worth of chemicals." Those things which our body is able to use are all soluble in water. Our digestive process is largely one in which starches, fats, and proteins are converted into water soluble substances which are then dissolved by the blood and, in turn, fed to the tissue and other cells. The oxygen which the body uses must also dissolve in the water of the body before it is of any use to us. Many of the waste products from worn-out tissues, too, are converted to water soluble material and eliminated in the water solution of the urine. In plants, water carries food from the soil into the roots and up through the entire cell structure. The process of photosynthesis, by which new plant tissues are formed, is carried out in the leaves in water solution.

Water which has been standing in contact with the soil for some time gets loaded with soluble material which is frequently of considerable economic importance. One big chemical company has been taking a million dollars worth of bromine a month out of sea water. This process of solution, then, results in the slow decomposition of certain rocks and indirectly leads to deposits of other material. Thus considerable quantities of limestone have been precipitated in pocket deposits from old sea water solution and many deposits of valuable minerals are thought to have been similarly concentrated.

It is also important that many chemical changes which take place slowly, if at all, under some dry conditions will occur quite rapidly if water is present. This may be because of the more intimate mixing which takes place in the solution and the fact that the reacting particles may be drawn together more readily.

Solutions are Mixtures. If salt is dissolved in water and we wish to separate the two we have to boil away or evaporate the water. Such a process is usually thought of as being merely one of physics with no chemical forces holding the water and the salt together. In the absence of chemical combination we can only say that solutions are surely mixtures. Another important fact is that if a solution is thoroughly stirred for some time, we may then analyze various portions of it and find that each portion has the same composition. This indicates that any one solution is homogeneous (i.e., the same) throughout. But two solutions made up from the same substances may be entirely different in their composition. Of course, there usually is a limit to the amount of a substance one may dissolve in another substance. In the light of these facts we may say that a solution is a homogeneous mixture whose composition may vary between certain limits.

Saturated Solutions. It is a common observation that there is a limit to the amount of salt which one may dissolve in a certain amount of water. Some other substances are scarcely soluble in water at all. Still others are extremely soluble. This is true of other liquids also. The liquid which serves to dissolve the other material is called the *solvent* and that which is dissolved is termed the *solute*. While solutions are not limited to solids and liquids at all but include every possible combination of solids, liquids, and gases, yet we shall consider a solid dissolved in a liquid as a typical example.

If water contains only a small amount of sugar it may be possible for it to dissolve still more. In this case the solution is said to be *unsaturated*. If to such a sugar solution one continues to add more and more sugar a condition is finally attained where no more of it will be dissolved and an excess will remain. Such a solution which remains unchanged in the presence of excess solute is said to be saturated.

Supersaturated Solutions. As a rule, the solubility of a solute in a solvent is increased with a rise in temperature and a warm solution can be made to contain more sugar than a cold one contains. If the hot saturated solution is freed from all excess of undissolved sugar and then carefully cooled it is quite possible that no solid sugar will separate even though the cold solution now contains more sugar than one can ever dissolve in the same amount of water without heating it. If, however, one adds a very small sugar crystal to the above cooled solution all of the excess sugar will separate out rapidly and a saturated solution will result. Such a solution which deposits some of the solute upon the addition of a trace of the solute is said to be supersaturated.

Colloidal Suspensions. The name, colloid, was originally given to certain gluelike substances. They are classed as colloids because of the size of the particles in solution. If one shakes a sample of ordinary sand with water it is to be expected that the sand will settle to the bottom of the container as soon as shaking stops. However, if the sand is ground to a powder this settling will go very slowly. Further grinding will so pulverize the sand that it will not settle to the bottom of the water until many hours have elapsed. Such mixtures in which visible particles are suspended in a liquid, are called *suspensions*. Your medicine, held in a bottle labeled "Shake well before using," is such a suspension. In many cases the particles may be so small that they become invisible to the naked eye and because of their size they do not settle out. They cannot be removed from the liquid even by filtering through an ordinary filter paper. Such suspensions as these are called *colloidal suspensions*.

Tyndall Effect. The fact that these colloidal suspensions contain small particles floating about in the liquid may be shown by passing a beam of light through them in an otherwise darkened room. The beam will pass through an ordinary solution without noticeable reflection if the eye is placed at right angles to the beam, but the passage of light through a colloidal suspension produces a slight cloud effect. The small invisible particles in suspension reflect the light which strikes them and we get an effect like that produced when a small ray of sunshine penetrates a dark room and is scattered by the dust particles in the air. This is called the *Tyndall Effect* after the English physicist who discovered it. This effect permits the examination of colloids with an ultramicroscope.

Colloidal suspensions play an important part in the natural processes of plant and animal life. The protoplasm which is the living matter of every animal cell is colloidal and the cell structure of plants is colloidal in nature also. Practically every life process such as nutrition, digestion, and secretion are processes

in which colloidal suspensions take part.

A list of the industrial fields involving colloids would pile up endlessly and would contain such items as the manufacture of rubber goods, textiles, paper, ink, photographic films, plastics, dairy products, varnish, salad dressing, and pottery. These constitute only a very few of the many colloidal industries. Very frequently we encounter colloids without recognizing them as such. We call some of them fog, smoke, glue, blue sky, and jelly. The field of colloids in chemistry is so great and its importance is so far reaching that it has become an almost separate field of study followed by thousands of men and women chemists the world over.

Solubility of Liquids in Liquids. It is common experience that many pairs of liquids are freely soluble in each other. We are all acquainted with such solutions as alcohol in water, glycerin in water, and various liquid hydrocarbons dissolved in each other as gasoline. If you wish to remove a drop of oil from a piece of clothing you will probably use a liquid such as carbon tetrachloride, or benzene, or gasoline to dissolve it.

If you send the garment to the cleaner that is what he will do. All of us know that the oil drop will not dissolve in water.

There is a common expression among chemists concerning the solubility of various liquids. We say that "like dissolves like." By this we mean that if the molecules of the two liquids are somewhat alike then they will dissolve each other. Suppose that we consider a few examples. There are a number of substances called alcohols which are becoming common commercial substances. Among these there are methyl alcohol (CH3OH), ethyl alcohol (C2H5OH), propyl alcohol (C₃H₇OH), butyl alcohol (C₄H₉OH), and amyl alcohol (C₅H₁₁OH). Let us consider the solubility of each of these in water. The water molecule may be written as HOH instead of H₂O. Now the formula of water looks like the formula for these alcohols in that all of them have an OH group. We find that the first three of these alcohols are quite soluble in water. Their molecules are not enough different from water molecules to affect the solubility. The fourth one, butyl alcohol, has a considerable amount of carbon and hydrogen and it looks still less like a molecule of water. We find that it is soluble in water to the extent of only about 8 percent. The fifth one which is still less like water is soluble in water to the extent of only 2 percent. All of these alcohols are soluble in each other.

An ordinary fat such as olive oil is made up largely of glycerin oleate, $(C_{17}H_{33}COO)_3C_3H_5$. You may see readily that this molecule is chiefly carbon and hydrogen. In order to dissolve it we should try some compound of carbon and hydrogen such as the hydrocarbons which are found in gasoline. At least one of these has the formula $C_{10}H_{22}$. This is a splendid solvent for olive oil. Its molecule is not too far different from the molecule of fat. You are probably acquainted with the fact that water and gasoline seem to be completely insoluble in each other. Their molecules are entirely unlike.

Those liquids which mix in all proportions are said to be *completely miscible*. Those which mix to a slight extent are said to be *partially miscible*, and those which fail to mix at all are said to be *immiscible*.

Solubility of Gases in Liquids. If you place a vessel of cold water on the fire and carefully observe it as it becomes warm you will notice the formation of bubbles within the liquid long before it has reached the boiling point. These bubbles are due to the dissolved air which escapes as the temperature rises. All gases are soluble in water to some extent though some are extremely so. You may recall that oxygen is more soluble in water than is nitrogen and that the air which is driven out of water by heat is richer in oxygen than is ordinary air. This dissolved oxygen is the only source available for the use of fish. Carbon dioxide is considerably more soluble in water than are such gases as nitrogen, oxygen, and hydrogen, but we have evidence that carbon dioxide reacts slightly with water to form carbonic acid. Ammonia and hydrogen chloride are extremely soluble in water. These in water form ammonium hydroxide and hydrochloric acid respectively. High solubility of any gas in a liquid leads us to suspect their chemical union.

Sometimes when you turn on a water faucet you are surprised to obtain a vessel of water which looks a little like milk. This soon clears and then is like any other sample of water. The milkiness is due to small bubbles of air which formed when the pressure on the water was released. This is an example of the effect of pressure on the solubility of gases in liquids. When you open a bottle of soda water which has not been cooled you expect to receive a stream of bubbles out of the bottle top. You merely release the pressure within the bottle and the carbon dioxide, which remained dissolved while under pressure, now largely becomes insoluble.

These observations just outlined embrace two fundamental

facts concerning the solubility of gases in liquids.

1. All gases become less soluble in liquids at higher temperatures. Unless the gas reacts with the liquid it is insoluble at the

boiling point of the liquid.

2. The solubility of a gas in a liquid at any temperature is proportional to the pressure applied to the gas. If the gas reacts with the liquid this statement is not true. In the case of a mixture of gases in contact with a liquid we find that each of

them dissolves independently of the others according to its own partial pressure.

Boiling Point of Solutions. If one heats a solution containing a solute such as sugar, which will not boil, until the solvent begins to boil away and then determines the temperature of the boiling liquid it is found to be higher than the boiling point of the pure solvent. From our earlier discussion (Chapter 9) it follows that the presence of the sugar must lower the vapor

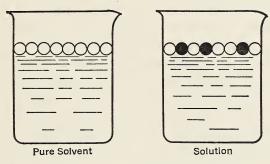


Fig. 28. The Surface of a Solution Contains Solute Molecules

pressure of the water and thus it is necessary to heat the water to a higher temperature before it begins to boil. We also have seen that the vapor pressure of the liquid is due to the more rapidly moving molecules leaving the liquid. Hence in order that the vapor pressure may be lower at a given temperature it is necessary that not so many molecules leave. This may occur for one or both of two reasons: the water molecules may be slowed down, or the surface may contain relatively fewer molecules of water. We have seen in previous discussions (Kinetic Theory) that the kinetic energy which the molecules possess is determined by the temperature only. Hence we must conclude that the solute may lower the vapor pressure of a solvent merely because it decreases the number of solvent molecules in the surface. This being the case there are fewer rapidly moving molecules available to evaporate.

It follows from what has gone before that the lowering of the vapor pressure of the solvent in a solution should depend upon the relative number of molecules of solvent and solute present. That this is true is shown by the fact that equal molecular amounts of various nonvolatile solutes dissolved in equal weights of water all produce the same elevation of the boiling point of the water. Thus 1000 grams of water to which has been added 1 molecular weight (342 grams) of sugar, or 1 molecular weight (92 grams) of glycerin will boil at 0.52° C. above the boiling point of water alone. Liquids other than water have their boiling points raised in a similar manner by the presence of dissolved material but the amount of elevation is not the same as that for water. For most common liquids this amount of elevation has been experimentally determined and put up in tables for us in our reference books. Use is made of this in the determination of the molecular weights of various substances. A known weight of a substance is dissolved in a known weight of water, or of other liquid, and the elevation of the boiling point determined. From this, together with the value of the molecular elevation for the particular liquid, the molecular weight of the substance may be quickly determined.

This behavior is summed up in the Law of Raoult which states that the rise in boiling point of the solvent in the solution is proportional to the number of molecular weights of solute present in a fixed amount of solvent. It must be remembered, however, that this refers to solutions of substances such as

sugar which do not themselves tend to boil away.

Freezing Point of Solutions. If one cools the solutions considered above, it is found that they do not freeze at the same temperature as that at which the pure solvent freezes but that they freeze at a lower temperature. Thus, if water is the solvent, the solutions of 342 grams of sugar or of 92 grams of glycerin in 1000 grams of water will each freeze at —186° C. Solvents other than water will have their freezing points lowered by other amounts. Here again equal molecular quantities of the solutes dissolved in identical amounts of the solvent, will produce equal effects. This behavior also becomes important in molecular weight determinations. In actual practice one never tries to freeze a solution containing such a large volume

of solvent but instead a small volume is used. In place of using enough of the solute to give a large lowering of the freezing point it is customary to use only enough to give about 0.1° lowering and to calculate the molecular weight from the data obtained. Such procedure is quite common in the chemistry laboratory.

The common practice in cold climates of putting antifreeze in a car radiator is a practical application of this principle. There are four leading antifreezes: methanol, alcohol, ethylene glycol and glycerin; and their molecular weights are 32, 46, 62, and 92 respectively. Thus for equal weights of the four those with lower molecular weights will produce the greatest lowering of the freezing point in the radiator. There are more molecules in a pound of methanol than there are in a pound of glycerin. This is largely offset by the low boiling points of the first two which cause them to be lost easily since they evaporate more rapidly than water does. You remember the boiling point elevation does not hold for such things as alcohol which boils quite easily.

Osmotic Pressure of Solutions. Osmosis is a common phenomenon but one which is little understood. It is by this method that water passes from the soil into the roots of plants. Many body processes, too, depend upon the transfer of water by osmotic means from one organ to another. Some idea of its nature may be obtained by finding out what may cause it. Let us imagine two vessels such as jars or glass beakers placed side by side, one containing pure water and the other a water solution of sugar. From our previous discussion it may be recalled that the vapor pressure of the pure water is greater than that of the water in the sugar solution, and thus, if these two solutions were allowed to stand long enough, the pure water would evaporate first. Instead of allowing these two solutions to stand in the open air suppose that we cover them both with the same jar turned upside down over them and seal its edges. The condition mentioned is illustrated in Figure 29. After some time the air in the inverted jar will contain quite a bit of water vapor. The molecules of water will be leaving the liquid and becom-

ing vapor and at the same time some water molecules will be leaving the vapor and becoming liquid. If we consider the sugar solution, however, we must remember that the vapor pressure of the water molecules in the pure water is greater

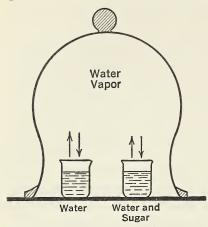


Fig. 29. Molecules Leave Pure Water and Enter the Solution

than the vapor pressure of the water in the solution. Water molecules will tend to leave the sugar solution more slowly than the pure water. Finally, water molecules will enter the sugar solution faster than they leave the sugar solution. In fact, the solution will drink up water from the moist air. So long as the pure water is present to furnish the molecules of water for the vapor this process will continue. After a time the volume of the

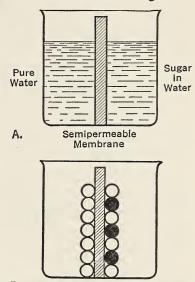
solution will be measurably larger. The greater the concentration of the solution the faster this process will take place.

Now let us transfer our idea of the two vessels containing water, and sugar in water, to a slightly different situation. This time we may consider the two liquids as being separated by an animal membrane such as the intestinal wall or bladder or a piece of parchment paper which will permit water molecules but not sugar molecules to pass through. Such a membrane is said to be *semipermeable*. The diagram (Figure 30) illustrates the idea more clearly. B shows a magnified portion of the picture as one may imagine it to be. The open circles represent water molecules and the dark circles represent sugar molecules. Now the number of water molecules passing through the membrane in either direction is proportional to the number of water molecules which get a chance at going through. Thus the pure water will pass through faster and will build up a larger (but more dilute) volume of solution. This net flow of

water into the solution may be stopped by the application of pressure to the solution and the pressure so required is called the osmotic pressure of the solution. It is obvious from the previous discussion that the number of molecular weights of

solute present in a given amount of solvent determines the osmotic pressure which results.

If two solutions of unequal concentrations are separated by a membrane within our bodies, the water will pass from the more dilute to the more concentrated solution. Two solutions whose concentrations give them the same osmotic pressure are said to be *isotonic*. The blood and the solution inside the blood corpuscles are isotonic. If the blood, for example, were replaced by water the water would enter the corpuscles and cause them to



B. Imaginary Magnification of above. The Water Molecules in the Solution have less Access to the Membrane

Fig. 30. Osmosis

burst. If the osmotic pressure of the blood were increased the water would pass from the corpuscles and they would shrink. Thus the injection of salt solutions into the blood stream to make up for lost blood must be carefully controlled.

SUMMARY

Homogeneous mixtures whose composition may be varied between certain limits are called solutions. These may consist of all possible combinations of solids, liquids, and gases.

The substance present in largest amount is usually termed the solvent, while that one which is dissolved is termed the solute.

A solution whose composition remains unchanged in the presence of an excess of solute is said to be saturated.

A solution which will dissolve still more solute if given a chance is said to be unsaturated.

A solution which will deposit some of the solute if placed in contact with a small bit of the solute is said to be supersaturated.

Solutions containing particles which settle out on standing are said to be suspensions. If these particles are too small to settle yet are not small enough to be in actual solution they are said to be colloidal. Colloidal solutions give the Tyndall effect when a beam of light passes through them.

The general rule that "like dissolves like" holds fairly well for the solubility of liquids in liquids. Liquid pairs may be classed as completely miscible, partially miscible, or immiscible,

depending upon their mutual solubility.

The boiling points of solutions containing nonvolatile solutes are higher than the boiling points of the pure solvents. The elevation of boiling point depends upon the relative numbers of molecules of solute and solvent according to the law of Raoult.

The freezing points of solutions are lower than the freezing points of the pure solvents and this, too, depends upon the relative numbers of solute and solvent molecules. Advantage is taken of this in the use of antifreeze in automobile radiators.

The elevation of boiling points and the lowering of freezing points furnish a means for the determination of the molecular weights of solutes.

Solutions exhibit what is called osmotic pressure. Pure solvent tends to pass through a semipermeable membrane into a solution so as to dilute it.

REVIEW QUESTIONS

1. Would you consider the great caves which exist in limestone formations to be due to removal of material by grinding away or by solution? Remember that the water flowing through such caves is usually quite clear and free from grit and sand.

2. Where do you suppose that the bromine now contained

in sea water came from? Where did the sea salt come from?

3. How do you account for the fact that the water flowing in the lower Arkansas River is usually too salty to drink?

4. You have seen the sediment contained in vessels used for boiling water. Where did it come from?

5. What do we mean by saying that a solution is homogeneous?

6. How can you increase the amount of sugar dissolved in a

given amount of water?

- 7. In making candy, why is it so necessary to use care while stirring? Why does it sometimes turn to sugar?
- 8. Ice cubes in a refrigerator may remain frozen while ice cream in the same compartment may melt. Explain.
- 9. The substance we use as cream is a colloidal suspension known as an emulsion. What are its two chief components? Are these liquids or solids?
- 10. You have probably seen a beam of light passing through a darkened room. Why does the beam look smoky or full of dust?
- 11. Suppose you were to spill motor oil on a garment. It is made up of molecules similar to $C_{14}H_{30}$. Which of the following would you use to remove it: water (HOH), alcohol (C_2H_5OH), or turpentine ($C_{10}H_{16}$)? Why?
- 12. For what reason should a bowl of goldfish not be placed in direct sunlight where it will get warm?
- 13. Suppose two eggs are being boiled; one is in pure water and the other is in water saturated with sugar. Which egg will get the hotter? Why?
- 14. Suppose you have two water pipes side by side in the wall of a house. One contains water which has been boiled but is now cooled, and the other contains unboiled water. Which should freeze first as the temperature drops? Why?
- 15. Which should lower the freezing point of a given amount of water more: one pound of methanol (CH₃OH), or one pound of ethylene glycol (C₂H₄(OH)₂)?
- 16. One car radiator contains 8000 grams of water and 2000 grams of methanol while another contains 8000 grams of water and 2000 grams of "prestone" (ethylene glycol). Calculate the expected freezing point in each case.
- 17. Using the density of water as 1, that of methanol as 0.8, that of glycerin as 1.26, and that of prestone as 1.1 calculate the weight of a gallon of each of these liquids.

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See also any text of General or Introductory Chemistry. A few of these are listed at the end of Chapter 8.

WATER: SOLUTIONS OF ELECTRO-LYTES. IONIZATION

Abnormal Solutions. When substances seem to behave in accordance with some general rule, chemists at once begin intense investigation. Many years ago there was much work done to see if all solutions behaved in the manner just described (Chapter 10). It was found that for a large group of solutes these principles hold rather rigidly, but another large group behaved peculiarly for the watching chemists. To the first group belong such substances as sugar, glycerin, and glucose, while to the second group belong such substances as salt, acids, and alkalies.

Electrolytes. Solutions of these abnormal substances in water were found invariably to conduct an applied electric current. But solutions of those considered as normal never conduct electricity. The molecular weights of these abnormal substances are known. But when a molecular weight (in grams) of one of them is dissolved in 1000 grams of water, the boiling point is raised more than 0.52° and the freezing point is lowered more than 1.86°. The osmotic pressure, too, is greater than it should be in a normal solution. It is quite interesting to add that the extra raising of the boiling point, lowering of the freezing point, and elevation of osmotic pressure are all relatively equal. The ease with which these same solutions conduct an electric current is likewise proportional to the extra elevation of the boiling point and lowering of the freezing point.

Solutions of Electrolytes React Rapidly. Those substances whose water solutions conduct an electric current are called electrolytes, and those whose solutions do not conduct a cur-

rent are termed nonelectrolytes. It is electrolytes we now consider. If we examine the chemical properties of solutions of electrolytes we find that they take part in chemical changes far more rapidly than do the dry materials. Two substances may be in contact without any chemical reaction taking place between them so long as they remain dry, but, as soon as they are placed in solution, and the solutions are mixed, a reaction takes place at a rate which is too rapid to be measured by any timing device. As you know, the dry materials in baking powder stay unchanged for a long time but the addition of water brings about an immediate formation of bubbles. A new storage battery for your car may come with dry chemicals. It does not begin to supply energy to turn the starter or to light the headlights until it has been filled with distilled water.

Behavior of Electrolytes Summarized. The general behavior of electrolytes may be summed up in three general statements.

1. Solutions of electrolytes exhibit abnormal elevation of the boiling point, abnormal lowering of the freezing point, and abnormal osmotic pressure.

2. Solutions of electrolytes will conduct electricity.

3. Electrolytes in solution will react together instantaneously while nonelectrolytes react slowly.

Theory of Ionization. Explanation by Arrhenius. A young Swedish student at Stockholm, by the name of Svante Arrhenius, offered an explanation for the above facts as early as 1885. Some of his conclusions were incomplete and others were wrong. By following his early thinking we can begin to understand his ideas. He thought that:

1. Molecules of electrolytes in solution are split apart into two or more particles which are electrically charged.

2. These electrically charged particles, called ions, carry the electric current through the solution.

3. Some of these ions have a positive electrical charge and others have a negative charge. The total positive charge is equal to the total negative charge and the solution as a whole remains electrically neutral.

4. The splitting apart of the molecules into ions is not complete but results in an equilibrium since the ions formed tend to recombine to form the original molecules. The amount of this splitting apart depends upon the substance, the amount of water present, and the temperature.

5. Chemical changes between electrolytes in solution take place between these charged ions rather than between molecules. Such reactions between charged particles take place in-

stantaneously; thus the rapidity of their union.

An Example of Ionization. As a practical example let us mix up a solution of water and common salt, which is sodium chloride (NaCl). Dilute water solutions of this material boil at a higher temperature than would be expected from the behavior of nonelectrolytes. A solution which contains 1 molecular weight (in grams) of salt in 1000 grams of water would be expected to boil at 100.52° but actually it boils at 100.97°. The elevation of the boiling point of the water is 0.97° instead of 0.52° and is therefore 1.84 times as great as expected.

If this same salt solution is frozen it is found that the freezing point is -3.42° instead of -1.86° as would be expected normally. Now 3.42° lowering is 1.84 times as great as 1.86°. As has been explained, it is the number of particles in solution which determines the elevation of the boiling point and the lowering of the freezing point and thus we must conclude that the salt solution contains about 1.84 times as many particles as would be expected if it were a normal instead of an electrolyte solution. A numerical example will make this more clear. Suppose that we start with 100 molecules of sodium chloride (salt) in solution and that 84 of these split to give one sodium ion and one chloride ion. Thus each molecule (or particle) which splits will produce two ions (particles) to take its place. The total number of particles in solution will become greater than the original number by the addition of the 84 extra ions produced. Written as an equation we have:

 $NaCl \leq Na^+ + Cl^-$. Particles at the start 100 Particles after splitting 16 84 84 = total of 184

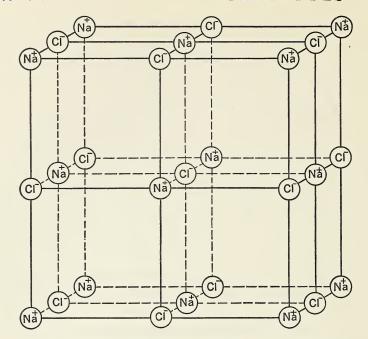


Fig. 31. Crystal Form of Sodium Chloride.

The solution just considered should behave as though it contains 1.84 times as many particles as it is supposed to contain if it were normal in behavior. If such a condition exists in the salt solution whose boiling point and freezing point were mentioned earlier then we may have a logical explanation of the facts observed.

Crystals of Salt Contain Ions. Since the time that the ionic theory was first proposed chemists and physicists have shown that crystals of sodium chloride actually contain sodium ions and chloride ions instead of molecules of sodium chloride. Thus in the crystal each sodium ion is surrounded by chloride ions and each chloride ion is surrounded by sodium ions. The fact that this is the case has caused some to wonder if sodium chloride molecules ever exist as anything other than a mixture of the charged ions resulting from the splitting of the molecules.

Theory of Complete Dissociation. Within the past few

years the theory of complete dissociation of electrolytes has been proposed and it is now generally accepted. It differs from the original ionic theory in that it assumes all electrolytes like salt to be completely ionized when in solution. We may then cite the fact that the salt solution previously considered boiled at 1.84 times as high as expected instead of twice as high. This is explained by proposing that these electrically charged particles influence one another and that there is a certain tendency for them to herd together so that they act as if they were only partially ionized. Now it is known that there is a force of attraction between positive and negative electricity. If a positively charged particle is present among negatively charged particles one would expect an attraction to exist between the positive charges and several negative charges. The same may be said for a negative charge among positive charges. The whole group of attracted particles may to some extent act as a unit and thus we get only the effect of partial dissociation instead of complete splitting into ions.

Naturally this effect of attraction would be expected to be greater in concentrated solutions than in dilute solutions simply because there are more particles in a small space and thus the electrical charges are closer together. As a matter of fact this is the case and in very dilute solutions we get the effect of complete ionization just because the charged particles are too

far apart to attract each other.

Acids, Bases, and Salts. According to the theory of ionization the reactions of electrolytes in solution take place between ions. In order to understand just what these reactions may be we need to know something about what ions may be present in a given solution.

Lavoisier probably was one of the first chemists to study the effect of water upon various substances. You may recall that he has been given credit for work on oxidation and combustion and that during the course of his work he observed the combination of most of the then known elements with oxygen. In many cases the products from this union (called oxides) would dissolve if he put them in water. The water solutions in some

cases took on a sharp taste together with other properties which are common to things we call acids, while in other cases certain properties characteristic of alkalies were noted. He classified the elements into two classes as a result of this. (1) Those elements whose oxides in water produced alkaline solutions he called metals and (2) those elements whose oxides in water produced acid solutions he called nonmetals. This classification of his has held to the present day.

Acids. The question of what gives the acid properties to certain substances puzzled Lavoisier. He thought it to be the element oxygen. Because he thought this he gave this element its name which means "former of acids." However, since his time it has been found that many substances containing no oxygen are also acids. Further studies and experiments have shown hydrogen to be the one essential element in all acids. They have revealed, too, that hydrogen ions bestow acidic properties upon any solution. Thus an oxide which gives an acid in water solution does so because it reacts chemically with the water to form a new compound which in turn ionizes to give hydrogen ions. For instance, carbon dioxide reacts with water to give carbonic acid which makes the bubbly gas in your soda water and pop. The chemical equation for this is written as:

$$\begin{array}{c} \mathrm{CO_2} & + \mathrm{\,H_2O} \rightarrow \mathrm{H_2CO_3} \\ \mathrm{H_2CO_3} \leftrightarrows \mathrm{H^+} & + \mathrm{\,HCO_3}^- \end{array}$$

That acids contain hydrogen may easily be shown by placing a piece of zinc or magnesium in an acid solution. The metal is dissolved rapidly and a stream of hydrogen gas bubbles out at the same time. Thus we say that the hydrogen is replaced by the zinc or magnesium. An iron nail will slowly dissolve in vinegar and hydrogen will be liberated in similar fashion.

Further proof of the presence of hydrogen ions in acid solutions is obtained by passing an electric current from a battery through them. In every case hydrogen is liberated at the negative terminal (electrode) in the solution. This shows that the acid hydrogen atom in solution is charged with the kind of

electricity which we call positive (+) and is therefore attracted to the negative electrode.

Acids Defined. Since it has been definitely established that acids are acids because of the charged hydrogen atoms which they give in solution we may use this in our definition. This particle of matter, called the hydrogen ion, which bears a single charge of positive electricity is called a *proton*. We may then say that an acid is anything which gives hydrogen ions (protons) when in solution. There seems to be no real reason for limiting ourselves to solutions and thus we may include all things which are able to supply protons under any conditions. An acid is a substance which can furnish protons.

Bases. Now let us turn our attention to that other class of substances, the alkalies, which result when metal oxides dissolve in water. After considerable experimentation it has been determined that these alkaline substances are all alike in that they contain oxygen and hydrogen linked together in what we term the *hydroxyl* group. Let us write the reaction equations for the formation of a few of these alkalies (bases) from the metal oxides.

CaO (calcium oxide) + HOH \rightarrow Ca(OH)₂ (calcium hydroxide) Na₂O (sodium oxide) + HOH \rightarrow 2 NaOH (sodium hydroxide)

Each of these hydroxides is alkaline in solution. They feel slick to the touch, have a caustic action, and change the color of red litmus paper to blue. These two given above are in common use. Calcium hydroxide is ordinary hydrated lime. It is used in the manufacture of paper, in mortar, and in plaster. Sodium hydroxide is called caustic soda. It is used in petroleum refining, in paper making, and in soap manufacture. The caustic properties are thought to be due to the hydroxyl ions which they give in water solutions. We may write the reactions of ionization using customary equations.

$$Ca(OH)_2 \leftrightarrows Ca^{++} + 2 OH^-$$
 (hydroxyl ions)
NaOH $\leftrightarrows Na^+ + OH^-$

For the present then we will say that all substances which give hydroxyl ions in solution are bases.

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Neutralization of Acids by Bases. Most of us know that acids and bases will neutralize each other. Before taking a used battery from a car the mechanic will usually wash it off with a dilute alkali solution. If you get caustic on your skin at home you will be urged to bathe the affected spot with vinegar or boric acid. In the presence of each other the acid and alkali seem to lose their characteristic properties. Let us write the equations which show the change which takes place. We shall use hydrochloric acid and sodium hydroxide as suitable examples. Hydrochloric acid ionizes in water to produce hydrogen ions and chloride ions. Sodium hydroxide ionizes in water to produce sodium ions and hydroxide ions (hydroxyl ions).

$$NaOH \hookrightarrow Na^+ + OH^-$$

 $HCl \hookrightarrow Cl^- + H^+$

Upon mixing solutions of these two substances there is a large amount of heat given off (13,700 calories for each molecular weight of NaOH). If we drive off the water which is present we find nothing left but common salt (NaCl).

To explain the facts involved it seems best to assume that everything which can happen will happen. When the two solutions are mixed we may expect that any positively charged ion may react with any negatively charged ion without preference. If Na⁺ reacts with OH⁻ we will get NaOH which will again ionize to form Na⁺ and OH⁻. Also if H⁺ reacts with Cl⁻ we will get HCl which will again ionize to form H⁺ and Cl⁻. If Na⁺ reacts with Cl⁻ we will get NaCl which will ionize to form Na⁺ and Cl⁻. If H⁺ reacts with OH⁻ we will get HOH (usually written H₂O) and this substance has been found not to ionize to any appreciable extent. When once formed, the water molecule stays together. We shall write all of these possibilities as equations with arrows to show the directions the changes may go.

$$\begin{array}{ccc} NaOH \leftrightarrows Na^+ & + OH^- \\ HCl & \leftrightarrows Cl^- & + H^+ \\ & & \downarrow \uparrow & \downarrow \\ NaCl & H_2O \end{array}$$

Careful measurements have shown that when once OH- and H+ get together they tend to stay together. While NaCl is completely ionized in water solution, it must be noted that water itself has only one molecule out of some ten million which is split into the ions H^+ and OH^- at any one time. Thus it is that the result of adding HCl to NaOH is the production of water together with the ions from common salt. If the water is removed by evaporation the salt separates out as crystals. The only change which occurred during the neutralization was the union of hydrogen ions with hydroxyl ions. The heat evolved was due to this union. Neutralization may be defined as the union of hydrogen ions from an acid with hydroxyl ions from a base.

Definition of a Base. In the light of the discussion just given it seems best to give a full definition of a base in terms of what it will do chemically. We have seen that some bases contain hydroxyl groups which will ionize. The hydroxyl groups which do ionize will combine with hydrogen ions (protons). We then may define a base as anything which will react with protons.

Neutralization Indicators. If we examine pure water we will find that it is neither an acid nor a base. It is neutral. Let us write the equation for its ionization.

$HOH \leftrightharpoons H^+ + OH^-$

From this we see that even though water does ionize to a very slight extent yet it produces equal numbers of hydrogen ions and hydroxyl ions. Thus neither can be in excess and the liquid is neutral.

There are many dyes and other colored materials which have certain colors in pure water and different colors in acids or still different colors in basic solutions. If one wishes to test a solution to see if it is acid, it is only necessary to dip a strip of paper, impregnated with the dye, into the solution. Many of us have tried the effect of saliva on litmus paper held within our mouths. If litmus turns blue it indicates alkali and if it turns pink it indicates acid. It is very convenient to use such a

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material to indicate when you have added enough acid to neutralize a base. Industrially, these indicators are used considerably. They are known as *neutralization indicators*. There are a great many of them and most of them fail to show the exact neutral point but they can be depended on to show the same condition every time and hence are useful.

Salts. We have defined acids and bases but there still remains a large group of substances which dissolve in water, to a greater or less extent, with the formation of ions other than H⁺ or OH⁻. Sodium chloride is typical of these. This substance in solution gives the negatively charged ions which came originally from the acid, and the positively charged ions which came originally from the base.

$$NaCl \Leftrightarrow Na^+ \text{ (from NaOH)} + Cl^- \text{ (from HCl)}$$

Such substances which give the positive ion of a base and the negative ion of an acid are collectively called salts. Thus NaCl is called common salt but it is only one of a large number of salts.

We have used examples of other salts in previous discussions.

$$\begin{array}{ll} \operatorname{FeSO_4} &\leftrightarrows \operatorname{Fe^{++}} \left(\operatorname{from} \ \operatorname{Fe}(\operatorname{OH})_2 \right) \ + \ \operatorname{SO_4^{--}} \\ & \left(\operatorname{from} \ \operatorname{H_2SO_4}, \ \operatorname{sulfuric} \ \operatorname{acid} \right) \\ \operatorname{ZnCl_2} &\leftrightarrows \operatorname{Zn^{++}} \left(\operatorname{from} \ \operatorname{Zn}(\operatorname{OH})_2 \right) \ + \ 2 \ \operatorname{Cl^-} \left(\operatorname{from} \ \operatorname{HCl} \right) \\ \operatorname{Na_2CO_3} &\leftrightarrows 2\operatorname{Na^+} \left(\operatorname{from} \ \operatorname{NaOH} \right) \ + \ \operatorname{CO_3^{--}} \\ & \left(\operatorname{from} \ \operatorname{H_2CO_3}, \ \operatorname{carbonic} \ \operatorname{acid} \right) \end{array}$$

We now assume that all of a salt which is in solution is completely ionized.

Some Ions Combine with Water. We are familiar with the fact that we can dissolve salt in water, then evaporate the water and get the salt back. There seems to be no other change. Experience has taught us, however, that molecules, or particles, which are different from either the water or the dissolved substance may exist in solutions. Ammonia is a gas and neither it nor water have any effect upon the color of litmus paper. If the two substances are placed together the resulting

solution has the properties of a base in water. The ammonia solution causes red litmus to turn blue indicating that ammonium hydroxide has been formed.

 $NH_3 + H_2O \hookrightarrow NH_4OH$ (ammonium hydroxide) $\hookrightarrow NH_4^+ + OH^-$

We can boil this solution and get back the ammonia, indicating that the ammonium hydroxide is an unstable compound.

Hydrogen chloride is a gas which has no effect upon litmus paper in the absence of water. When the gas is dissolved in water there is the evolution of considerable heat. This you remember is an indication of a chemical change. The resulting solution is a strong acid but we can get no special compound out of it which indicates that it has reacted with the water. There are many reasons for assuming that water does react with hydrogen chloride, however. The generally accepted reaction is one of *hydration* of the proton from the hydrogen chloride.

$$HCl + H_2O \Leftrightarrow Cl^- + (H_5O^+)$$
 (hydronium ion)

This hydronium ion is nothing more than a hydrogen ion in combination with a molecule of water.

$$H^+ + H_2O \leftrightarrows (H_3O^+)$$

We assume that this hydronium ion can give up protons and therefore act as an acid.

Copper sulfate is a white substance with the formula CuSO₄. When placed in water it gives a pale blue solution. If the water is evaporated we obtain crystals having the deep blue color of the substance we know as "bluestone." By means of analysis the formula for these crystals has been found to be CuSO₄ (5H₂O). For each molecule of copper sulfate there are five molecules of water. This water may be removed by heating the crystals to 200° C. for a few hours and the original copper sulfate obtained.

When sodium hydroxide is placed in water it causes the evolution of enough heat to boil the water. The resulting solution gives no indication of the presence of any new substance. We can only assume the occurrence of some sort of reaction be-

tween the ions from the sodium hydroxide and the molecules of water. The heat evolved surely indicates such a change.

Sulfuric acid dissolves in water with the liberation of much heat. Unless great care is used in mixing these substances the solution is apt to boil suddenly with the production of steam which throws out some of the acid. There is evidence for the formation of a definite compound H₂SO₄(2H₂O).

Heat Changes Accompany Ionic Reactions. There is every reason to assume that heat changes occur when ions react. The heat effects noted in the previous section furnish evidence for this. Let us return to the neutralization of an acid by a base and write a few of the equations. We shall assume the acids and the bases to be completely ionized and shall write the ions separately.

$$\begin{array}{c} Na^{+} + OH^{-} + H^{+} + Cl^{-} \rightarrow Na^{+} + Cl^{-} + H_{2}O + 13,700 \text{ calories} \\ K^{+} + OH^{-} + H^{+} + Cl^{-} \rightarrow K^{+} + Cl^{-} + H_{2}O + 13,700 \text{ calories} \\ 2Na^{+} + 2OH^{-} + 2H^{+} + SO_{4}^{--} \rightarrow 2Na^{+} + SO_{4}^{--} + 2H_{2}O + 27,400 \text{ calories} \end{array}$$

It will be noticed that for every molecular weight of water formed from the ions, H⁺ and OH⁻, there is the evolution of 13,700 calories of heat. This results from the union of the two ions. The ions of the salts formed stay in the ionic condition and contribute no heat.

Since the union of ions produces the evolution of heat it seems safe to assume that the separation of ions involves the absorption of heat. If we place a substance in water, and as a result it splits apart into ions, we should expect a cooling effect. This is frequently noticed. Many times, however, the resulting solution gets warm, as has been noted. This is explained by assuming that the ions formed react with the water molecules to form *hydrates*. Using HCl as an example we may write an equation.

$$HCl (un-ionized) + H_2O \Leftrightarrow Cl^- + (H_3O)^+ + heat$$

The heat which is evolved is only the difference between that required to ionize the HCl and that liberated by the union of H⁺ and H₂O to form (H₃O)⁺.

Freezing Mixtures. When you buy ice cream for a picnic you may expect to keep it for some time before serving it. If the one who packs it does not have dry ice he will use a mixture of ice and salt to keep it cold. Possibly you prefer to freeze your own. In this case you may produce the freezing with a mixture of salt and ice.

It has been pointed out that a solution freezes at a lower temperature than does the pure solvent. If we place salt on ice it produces a little of a salt solution with the water which is present on the surface of the ice. We then have a salt solution in contact with ice. Ice and water can exist together at 0° C. without either of them changing, but if salt is present in the water the mixture must be much colder if the ice and solution are to remain together without changing. The ice begins to melt and passes into the salt solution. Now you may remember that to melt a gram of ice requires 79 calories of heat. The melting process which takes place absorbs heat wherever it may and as a result the ice cream mixture is cooled. Most any other salt may be used unless it reacts with water with the production of heat.

SUMMARY

Solutions of electrolytes possess properties which are not exhibited by solutions of nonelectrolytes. Such solutions freeze abnormally low, boil abnormally high, have abnormally high osmotic pressure, conduct an electric current, and give instantaneous chemical reactions.

Arrhenius proposed that electrolytes in solution are ionized to give particles bearing electric charges; some positive and some negative. The abnormal properties of these solutions are due to the abnormal number of these particles and to their electrical charges.

On the basis of crystal structure and other evidence it is assumed that certain electrolytes are completely ionized even in the crystal form. Electrolytes in solution sometimes appear not to be completely ionized due to the herding together of the charged particles by reason of their charges.

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Acids are substances which are able to furnish protons. Bases are substances which are able to unite with protons.

The neutralization of an acid by a base is essentially due to the union of protons from the acid with hydroxyl ions from the base with the formation of molecules of water which are not ionized. The other product of a neutralization is a salt.

Some ions react with water, with the evolution of heat, to form hydrates. The water of hydrates may usually be driven off by heating them.

When ions react with other ions a heat change occurs.

When electrolytes are placed in water there is usually a heat change which may be a loss or a gain. It represents the difference between the heat of hydration of the ions and the heat required to cause solution and ionization.

REVIEW QUESTIONS

- 1. Why are certain substances called electrolytes?
- 2. For what reasons do we say that solutions of electrolytes are abnormal?
- 3. Summarize the theory of ionization. In what ways does this account for the abnormalities of solutions containing electrolytes?
- 4. What appears to determine the amount of freezing point lowering produced on a solvent by a solute?
- 5. Why do electrolytes in concentrated solutions appear to be less ionized than in dilute solutions?
 - 6. Define: acids, bases, salts.
- 7. How may you demonstrate the presence of hydrogen in acids?
- 8. Upon what was the original classification of metals and nonmetals based?
 - 9. What essential change occurs during neutralization?
 - 10. Why is pure water neither acidic nor basic?
 - 11. Give some evidence that ions may combine with water.
- 12. Are the unions of ions with water chemical or physical? Are these unions difficult to break down?
- 13. What name is given to the substances formed by the union of ions with water?
 - 14. Why does a mixture of salt and ice get cold?

15. Suggest an easy method for the removal of ice from a door-step or walk.

16. What is the connection between the freezing of ice cream and the melting of the ice which surrounds it?

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- See also any text of General or Introductory Chemistry. A few of these are listed at the end of Chapter 8.

WATER PURIFICATION

The preceding discussions have emphasized how important a part water plays in chemical changes, but to many this type of importance seems to be secondary. Actually, there is no chemical substance of greater economic value, nor of greater importance to life than is water. Modern city life demands that a suitable supply of this liquid be available at all times for human, animal, and plant drinking, for washing, for sewage disposal and for a thousand other uses. To make it available there are untold millions of dollars invested in water supply equipment all over the world. To read the figures which give the quantity of water consumed each day in a large city causes us to wonder how so much can possibly be used.

Requirements for Water Supply. Regardless of the source from which a water supply is obtained — whether from lakes, running streams, deep artesian wells, or storage cisterns — there are certain requirements which must be met by the water which is delivered to the consumer. The water so delivered must have a clear, sparkling appearance and be free from color or objectionable odor. It should taste good, be safe to drink, and be free from poisonous chemicals or disease bacteria. For most cities the water should be suitable for use in steam boilers. Of course, we may put our own individual values upon these requirements, but it is the public duty of a water company to supply water fit for human consumption. And if the other things such as clarity and tastiness are possible to attain the water becomes that much better.

What Constitutes Good Water. In order to determine what constitutes good water we must consider several factors. Water which has been in contact with the soil is sure to contain

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chemical substances dissolved from the soil. Thus the nature of the water will largely be determined by the chemical makeup of the soil in any particular locality. Some water sources may contain enough common salt to render them unfit for human consumption. But such unfitness is a matter of how the taste affects the tongue and the emotions rather than any really ill effects upon our bodies and our health. On the other hand there are many things which may be present in amounts too small to detect by taste and yet render the water mildly poisonous or productive of sometimes fatal disease. Or again, certain chemicals may neither poison nor make us ill but have an unwanted effect. It now seems fairly certain that continued use of drinking water which contains sodium fluoride will cause a child to have darkened permanent teeth at a later date. The presence of this substance in their source of supply is causing some towns to consider other water sources to meet their needs.

The most important ill result of bad water is that it carries disease. Experience has shown that there are three main types of disease which may be carried by water. These are (1) typhoid fever, (2) some types of dysentery, and (3) Asiatic cholera. For years this silent carrier of typhoid fever has been a major factor in human life all over the world. During the "Century of Progress" fair in Chicago an outbreak of amoebic dysentery caused by sewage getting into drinking water demonstrated the dangers that can strike through the water supply even in our more or less efficient modern American civilization. History is filled with the ravages of cholera spread in the same way through the Orient.

The Purification of Water. Many cities must depend on a river for their source of supply, but some are fortunate enough to have access to a lake or to deep wells. The most desirable situation is one in which the water comes from mountains which are far removed from points of contamination. But such conditions are hard to find, and no city dares to depend upon the natural and unguarded purity of such water even if they have it. Ordinarily a city finds itself forced by geography or

costs to use the water nearest at hand. When the mineral content is too great and it cannot be removed satisfactorily, or the cost of removal is greater than that of bringing in a supply of purer water from a great distance the source of supply may be changed. Usually, however, the source of supply is found to be polluted, but methods of treatment make possible the removal of harmful germs. Whenever a river supply is used there is the almost ever present fact that the same river has

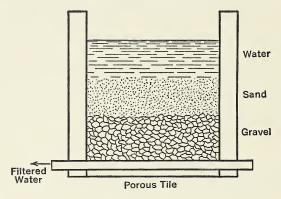


Fig. 32. A Rapid Sand Filter

served to wash away the waste from some city farther up the stream.

The general treatment given to ordinary water supplies is more or less the same all over the world. If necessary, the water is first run into a large basin or reservoir where the dirt settles to the bottom during the course of a few hours or a few days depending upon how much and what kinds of dirt are present. Considerable colloidal matter, bacteria, color, and odor may still persist. Further standing will have little effect upon these things. The partly clarified water may then be ready for filtration. But to remove properly enough of the suspended matter would require thick filters and such a long time for the water to seep through that large amounts of it could be supplied only with difficulty. However, if the water is treated with alum it forms a flocculent (feathery) precipitate which carries most of the dirt and most of the bacteria to the bottom with it

leaving comparatively pure water towards the top. The alum which furnishes the aluminum ion (Al⁺⁺⁺) reacts with the (OH⁻) ions of the water to produce a white gelatinous substance, aluminum hydroxide. The chemical reaction is written:

$$Al^{+++} + 3OH^{-} \rightarrow Al(OH)_{3}$$

If the water does not contain enough of the (OH⁻) to produce the precipitate it may be made to do so by the addition of lime which is calcium hydroxide Ca(OH)₂.

After permitting most of the aluminum hydroxide to settle out, the water is run onto and down through a rapid sand filter which consists of about twenty inches of fine sand supported on a like amount of graded gravel. The remaining flocculent material forms a very efficient coating on the sand to trap further dirt and germs. Water so filtered is remarkably clear and free of most of the bacteria. As the filters become dirty they are washed by forcing clear water through them from below and then draining the dirt to the sewer.

In order to free this clarified water of all remaining bacteria, it is treated with chlorine gas or other suitable germicides. Most water supply plants use chlorine, either alone or mixed with ammonia which seems to permit higher concentration of chlorine without making the water unpleasant to taste and permits the action of the chlorine to persist even in the mains. The chlorine reacts with the organic matter present and converts it to harmless material. Since the amount of organic material in the water may vary from day to day, it is very necessary that a constant check be made in order that sufficient chlorine may always be added to destroy all bacteria. Since we began to use chlorine to purify our water in this country, the death rate from typhoid fever has dropped markedly, and some of our large cities can point to several years with no typhoid deaths at all.

Certain sections of the country experience much trouble with unpleasant tastes and odors in the water. For years the removal of these has been difficult. Frequently the smell has been partially removed by spraying the water in the air, but this treatment is not always satisfactory. Within the past few years "activated" charcoal has been used in large amounts to remove both color and odor. Its use has been highly successful. It is added to the water before filtration and is removed along with the absorbed color and odor by the subsequent filtration process. This charcoal is made from wood by a special process and is ground to a small size. If one of the small pieces is magnified it resembles a sponge in appearance and presents an extremely large surface. Colors and odors are adsorbed (stick to) on this surface and are thus removed from the water. This is much like the similar use of charcoal to filter air in the use of gas masks.

Hardness. Water which contains soluble compounds of calcium and magnesium is called hard water. The term hardness refers to the effect which such substances have upon soap. Soap is the sodium salt of certain organic acids which are obtained from fats. The property of producing a lather is limited to a few such substances. It so happens that the potassium salts of these same acids are also soaps which will produce a lather. However, if certain other metal ions are substituted for the sodium in soap, the salt so formed is not soluble in water and possesses none of the properties usually associated with soap. Thus if a sodium soap is added to water which contains calcium ions, the soap is removed by the formation of an insoluble calcium compound; which sometimes explains the ring on the bathtub. It is only after the complete removal of the calcium ions that a lather may be produced.

In order to make this more clear we may write the chemical equations. Soap may be assumed to be sodium oleate (C₁₈H₃₃ O₂Na) and since it is a salt it will be ionized in water solution as follows:

$$C_{18}H_{33}O_2Na \Leftrightarrow C_{18}H_{33}O_2^- + Na^+$$

Since calcium chloride is also a salt it too will be ionized.

$$CaCl_2 \leftrightharpoons Ca^{++} + 2Cl^{-}$$

The two of these present in the same solution will react in every way possible. But since calcium oleate is insoluble this substance will be formed in preference to anything else.

$$\begin{array}{c} 2C_{18}H_{33}O_{2}Na \leftrightarrows 2C_{18}H_{33}O_{2}^{-} + 2Na^{+} \\ CaCl_{2} \leftrightarrows Ca^{++} + 2Cl^{-} \\ \downarrow & \downarrow \uparrow \\ \underline{(C_{18}H_{33}O_{2})_{2}Ca} & 2NaCl \\ \underline{insoluble} \end{array}$$

Thus one may see that soap is used up in the removal of calcium ions from the water and after the complete removal of such ions additional soap will produce a lather. Similar results are obtained from any calcium or magnesium compound which may be dissolved in the water.

There are also other disadvantages of hard water. Steam boilers filled with such water give a great amount of trouble. During the early days the railroad engines crossing the midwestern plains used the water present at towns or water holes along the line. But it was soon found that the substances present in much of this water destroyed the boilers. Either the compounds present reacted with the hot water to dissolve the iron of the boiler tubes so that they leaked like sieves, or the hardness compounds precipitated out of the water and coated the tubes with hard boiler scale. This scale formed thickest where the fire was the hottest. Sometimes the scale cake got so thick it clogged the boilers and the pressure burst them.

In addition to these objections to hardness, there are others of commercial importance. There are many industries such as dyeing, papermaking, brewing, food packing, and drug manufacture, which must constantly watch their water supply and control its mineral content.

Removal of Hardness. In general there are two types of water hardness, permanent and temporary. Permanent hardness is due to the presence of the chlorides or sulfates of calcium or magnesium (CaCl₂, CaSO₄, MgCl₂, MgSO₄). This type of hardness may be removed by the precipitation of the calcium and magnesium ions by the addition of the proper

chemical substances. Of course, we could use soap as has been pointed out, but such procedure would be entirely too expensive. Moreover other substances which cost much less are even more effective than is soap. Ordinarily one finds sodium carbonate (sal soda), sodium phosphate, or borax for sale as water softeners. Let us look at the action of the first of these. Sodium carbonate in solution is ionized and the carbonate ion (CO₃—) reacts with any calcium ions (Ca⁺⁺) to form the insoluble compound calcium carbonate (CaCO₃).

$$\begin{array}{c} CaSO_4 \leftrightarrows Ca^{++} + SO_4^{--} \\ Na_2CO_3 \leftrightarrows CO_3^{--} + 2Na^+ \\ \downarrow & \downarrow \uparrow \\ \underline{CaCO_3} & Na_2SO_4 \end{array}$$

The insoluble calcium carbonate may be removed by filtration, or it may be allowed to settle so that the clear liquid may be poured off. The price of soap may be twenty cents or more per pound, while the sodium carbonate required may be purchased for two or three cents per pound. This, together with the fact that one pound of dry sodium carbonate can soften as much water as six pounds of soap, makes obvious which is better.

Temporary hardness is caused by the presence of calcium and magnesium bicarbonates in the water. When the water in the soil comes in contact with the air it dissolves carbon dioxide to form a weak acid known as carbonic acid (H₂CO₃). Frequently this slightly acid water comes into contact with limestone (CaCO₃), or marble (CaCO₃) and some of the stone dissolves to form calcium bicarbonate (Ca(HCO₃)₂).

$$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$$

The reaction is reversible. Hence, if the water solution is boiled, the carbon dioxide is removed and the calcium carbonate precipitates out.

The removal of temporary hardness may be brought about by boiling the water. Most of us have boiled water many times in a kettle or pan and have seen the deposit of scale which results from the precipitation of calcium carbonate. Naturally, however, such removal as this cannot be applied to large-scale chemical and manufacturing operations.

Like permanent hardness, temporary hardness may be eliminated by soap and other methods similar to those used to rid water of permanent hardness. There is one point of difference, however. This arises from the carbonic acid which dissolved the limestone or other carbonate in the first place. If this acid is neutralized the carbonate will precipitate. One of the cheapest alkalies is lime (Ca(OH)₂). If this is added to the water containing temporary hardness the water is softened.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$

It will be noticed that the calcium added in the form of lime is also precipitated as the carbonate. If an excess of lime is added the calcium will cause the water again to become hard.

In ordinary practice both kinds of hardness occur together. Hence, large-scale softening plants use a correct mixture of lime and sodium carbonate. This constitutes the usual method employed by the railroads and plants using steam or hot water boilers. Billions of gallons of water are softened in this way each year. The chemical control of the process must be fairly exact, and large amounts are spent on equipment and for chemicals. But the process results in savings of millions of dollars in upkeep and replacement of costly machines. Such treatment is largely confined to the central and southwestern states.

Within recent years a similar method has been developed to soften water for use in the home. This consists in the installation of a tank through which all the water entering the house must run. The tank is partially filled with a solid which is essentially sodium aluminum silicate (NaAlSiO₄). This may be either a naturally occurring mineral or a manufactured substance. The natural material is called *zeolite* and one manu-

factured product is called *permutit*. When hard water passes through this mineral a chemical change occurs which exchanges sodium for calcium or magnesium.

$$2 \text{NaAlSiO}_4 + \text{CaSO}_4 \rightarrow \text{Na}_2 \text{SO}_4 + \underbrace{\text{Ca(AlSiO}_4)_2}_{\text{(insoluble)}}$$

The insoluble calcium aluminum silicate remains in the tank and the small amount of sodium sulfate that is picked up by

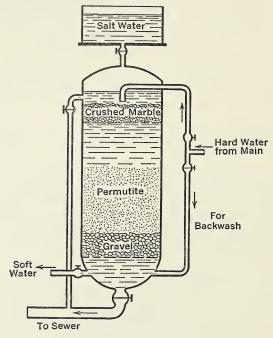


Fig. 33. A Home Water Softener

the water does no harm. This method of softening water is made not too difficult for the household by the fact that the mineral in the tank may be regenerated by treating it with a strong salt brine for a few minutes and then washing away the excess salt and calcium chloride.

$$Ca(AlSiO_4)_2 + 2NaCl \rightarrow 2NaAlSiO_4 + CaCl_2$$

Softening of City Supplies. More and more, there is a demand for soft water. Private installations in the home are rather expensive, but they give a very soft water if properly cared

for. Some cities have already attempted to answer the demand for soft water and are removing at the filtration plant at least some of the hardness which is present. But since much of the total consumption is used for irrigation, watering lawns and flowerbeds, street washing, fire fighting, and sewage disposal it is obviously costly and unnecessary to remove all the hardness. It is probable, however, that the demand for some inexpensive softening will grow and that many more cities will undertake it as soon as the consumers let their wants be known.

Safeguarding Our Water Supplies. In the ordinary course of events the treatment given the water in the average city is sufficient to insure the delivery of good water to the user. Even the untrained are able to complain if their drinking water is cloudy, or if it has a bad taste or odor. There are things, however, which give no warning of their presence; these are the germs of dreaded disease. They should not be present in treated water but you never know when something may go wrong. Men and machines do not always perform perfectly. Because of this it is quite necessary that some trained person shall be on the alert always for signs of contamination in the water system. It is not only necessary to kill the bacteria and keep new ones out of the system but it is just as necessary to destroy the food required for their growth and multiplication.

The chemist must cooperate with the bacteriologist in the detection of microscopic organisms. Small samples of water are diluted and mixed in flat dishes with gelatin or agar containing food on which bacteria may live. The gelatin or agar forms a firm, moist base upon which the organisms may establish themselves and begin their process of multiplication. If the dilution has been great enough, these organisms will be spread out so that they do not interfere with each other. After a day at body temperature, in an incubator, each original organism is surrounded by a whole group of other organisms, its prog-eny, and the group (colony) is large enough to be seen. By counting the number of colonies in one dish it is quite simple to state the number of organisms originally present in each milliliter of water. Each organism has developed a colony of its own. An experienced worker is able to tell something about the type of organisms by the color, shape, and size of their colonies. An appreciable number of bacteria of any sort, whether harmful or not, indicates incomplete treatment of the water or additional pollution after treatment.

It is of particular interest to determine if the organisms present are among those which live in the bodies of warm-blooded animals. The organisms which cause typhoid fever, dysentery, and cholera are difficult to detect in water. Coliform organisms live and grow in the intestines of men and other animals and these may be detected quite easily. If these are found in the water it may be presumed that the water is being contaminated by human sewage and thus may serve as a source of disease. These bacteria are detected by their ability to bring about the fermentation of a beef extract broth which contains lactose (milk sugar).

Samples of water for bacteriological examination are taken several times each day from various points throughout the system in our larger cities. Smaller towns do not as a rule maintain such constant control but do examine samples quite frequently. It sometimes becomes necessary to add a large excess of chlorine to the water at the pumping plant in order that the water everywhere in the system may be kept safe. Private water systems are frequently connected to the water mains and due to pressure changes the private source feeds into the mains. The next time you taste or smell chlorine in your drinking water you may remember that it is better to drink a little chlorine, which is harmless at such dilution, than to have typhoid fever. The fact that the city has not known typhoid fever for ten years does not make the water safe now.

The water chemist is constantly on the alert for signs of sewage contamination in water. This applies not only to city supplies but also to wells and springs throughout the country. All sewage is heavily charged with nitrogen compounds. These are classed as: albuminoid ammonia, from fairly fresh sewage; free ammonia, from partially decomposed sewage; nitrites, from less recent pollution; and nitrates, from fully oxidized

sewage. The tests for these indicate a great deal about the recentness of the pollution and help to determine the source.

There are still other tests to be made on water. The total amount of solids in suspension as well as in complete solution has quite a bit to do with the usefulness of the water. The hardness and whether it is temporary or permanent determines the amount of soap which must be used and also the amount of softening required by laundries and industries. In certain sections of the country the water becomes acid due to drainage from mines and from factories. Such water destroys the pipes through which it is pumped and calls for treatment with calculated amounts of lime. Even the fish are protected by chemical control. There are laws which have to do with the pollution of a stream by a factory. If the material fed into the stream uses up the oxygen it will cause the fish to die. The water chemist must look after this pollution for the protection of the stream and the industry.

SUMMARY

The water supplied to a city must be free from disease-producing bacteria. It must contain no harmful chemicals and must be pleasing in appearance, taste, and odor. In most cities it must also be suitable for industrial use.

The bacteria carried by water are those of typhoid fever, dysentery of certain types, and Asiatic cholera. The purification process must remove these and other bacteria as well as the food they live on.

The purification of water, in general, involves the removal of dirt by sedimentation. This is followed by the addition of a flocculating agent such as alum, with subsequent filtration through sand. Escaping bacteria and organic matter are destroyed by the addition of chlorine to the filtered water. Odor, tastes, and color are removed by treatment with charcoal prior to filtration.

Hardness in water is either temporary or permanent. Temporary hardness is due to the bicarbonates of calcium and

magnesium. Permanent hardness is due to the chlorides and sulfates of calcium and magnesium.

The removal of hardness may be accomplished by the use of soap which precipitates the calcium and magnesium ions. This may be done more cheaply by the use of sodium carbonate, borax, or sodium phosphate. Temporary hardness may be removed by boiling or by the addition of the correct amount of lime. Home water softeners may contain zeolite or permutit. These are regenerated by the use of a concentrated solution of common salt. Some cities are installing plants to remove most of the hardness present in the water which they use.

REVIEW QUESTIONS

- 1. What are the requirements for a good water supply?
- 2. What diseases are generally considered to be carried in water?
- 3. By what means are most of the dirt and bacteria removed from water?
 - 4. Describe the construction of a water filter.
- 5. What name do we give to a reaction in which the ions of water take part?
- 6. For what purpose is chlorine used in water? Why is ammonia used with it?
- 7. Give the causes of the two types of hardness. What is their effect with soap?
- 8. How may the hardness of water be removed? Explain fully with equations.
 - 9. By what means are bacteria in water detected?
- 10. What significance is attached to the presence of coliform organisms?
 - 11. Why are fish killed by excess organic matter in streams?

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SALT—CLASSIFICATION OF THE ELEMENTS

Ordinary salt is one of the most common, and one of the most important, substances which we know. It is almost impossible to estimate the amount of it which is present on, and in, the earth where man may reach it. About 3.5 percent of the weight of ocean water is due to this substance in solution. There are enormous beds of rock salt underlying portions of the land in various countries. Many deep wells are drilled into underground streams of salt-laden water. These sources of salt do not furnish pure material by merely evaporating the water, or by digging into salt rock deposits. But it is rather easy to prepare a product from either of these which is pure enough for most of our needs.

In the minds of many, salt is associated only with human wants for savoring food. Man and most other animals crave and need salt as a part of the diet. Medical science knows that it contributes a vital part to the digestive process as well as to the general functioning of the body. However, in the number of total tons of salt used by man, its function with food is minute in comparison with its use in the manufacture of other things. In its common kitchen or ice-cream freezer form, salt has very few uses. But, if it is used as a raw material and subjected to chemical changes, the products which may be formed are numberless. In fact, they touch nearly everything with which we come in contact. And yet these uses are comparatively recent. A process for making soda ash (sodium carbonate) from salt was perfected about 1791. Since that time salt has become an increasingly important raw material.

Before we can learn much of these chemical changes which

widen the scope of salt's usefulness to men, we must get a better conception of the nature of the salt molecule and the parts of which it is composed. It has already been pointed out that salt may be formed by the union of hydrochloric acid with sodium hydroxide. This has been written as follows:

$$\begin{array}{c} HCl \leftrightarrows H^+ \ + Cl^- \\ NaOH \leftrightarrows OH^- + Na^+ \\ \downarrow \qquad \qquad \downarrow \uparrow \\ H_2O \qquad NaCl \end{array}$$

We explained that this process is one of neutralization and is similar to that which occurs between any acid and any base. In every such case one of the products is water and the other product is a salt. While kitchen salt is just one of this entire class of salts we can continue our practice of simply calling it salt, with full knowledge that it is only one, although the most common, of a whole class of chemical compounds.

The Charge on the Ions. We have written equations which represent the ionization of salt and other substances. But nothing has yet been said about how it is possible for such a thing as an ion to exist. If we place sodium on water we find that it reacts at once to liberate hydrogen from the water. The reaction is so violent that the hydrogen catches fire if the sodium is confined to one spot. On the other hand, chlorine is a highly poisonous gas which slowly reacts with water under the proper conditions to produce a little oxygen. It seems certain, then, that a salt solution does not contain free sodium atoms and chlorine atoms floating about in the water. The difference must be in the electrical charge which is attached to these atoms in the solution. This electrical charge seems to confer unusual properties on the atoms which are so charged. Sodium will react with chlorine to form a salt and this salt dissolves in water to give the charged ions Na⁺ and Cl⁻. Evidently, then, the positive and negative charges come into evidence during the chemical reaction, and some relation must exist between electricity and chemical combination.

Review of Electrical Terms. Before proceeding further we must review some electrical terms. Electricity can be made to

flow through a conductor provided an electrical pressure is applied. Just as water under pressure will flow through a pipe, so electricity will flow through a conductor if an electromotive force, or a difference in voltage, exists between its two ends. The rate of flow depends upon this electromotive force and upon the size of the conductor as well as upon the ease of flow through the conductor. The unit of electricity is called the coulomb. This is a definite quantity just as a quart of a liquid is a definite quantity. This quantity of electricity may flow rapidly or it may flow slowly. If it flows in one second through a conductor, we say that the current is one ampere. The unit of resistance is called the ohm. A column of mercury which is one square millimeter in cross section and 106.3 centimeters long has a resistance of one ohm if the temperature is 0° C. If one volt is applied to this column of mercury, one coulomb of electricity will flow through it each second.

The first source of current electricity was made available just prior to 1800 and soon afterwards various experimenters began to investigate its chemical effects. In 1807, Sir Humphrey Davy passed electricity through some melted potassium oxide, and, at the negative electrode, he found the element potassium. In a similar manner he prepared the elements sodium, barium, calcium, strontium, and magnesium. This showed that some connection must exist between electricity and chemical combination.

Electrolysis of Solutions. Michael Faraday studied the effect of electricity upon solutions of electrolytes. He measured the amount of electricity which he passed through various solutions. Then he weighed, or otherwise measured, the amounts of material set free at the electrodes. When the solution consists of an acid, such as sulfuric acid, dissolved in water, the passage of the current liberates hydrogen at the negative electrode and oxygen at the positive electrode. This phenomenon has been described earlier. Faraday found that, in order to liberate one gram-atomic weight (1.008 grams) of hydrogen, it was necessary to pass 96,500 coulombs of elec-

tricity through the solution. This was observed to be an exact quantity. Any larger or smaller amounts of hydrogen liberated always required a proportionately larger or smaller amount of electricity.

By changing the electrolyte to copper (cupric) chloride, it was found that careful control of the current would deposit only copper at the negative electrode and that no hydrogen would be released from the water. In this case the amount of electricity consumed was $2 \times 96,500$ coulombs for each gramatomic weight (63.57 grams) of copper liberated. In another experiment a solution of gold chloride was electrolyzed. In this instance it required $3 \times 96,500$ coulombs to liberate a gram-atomic weight (197.2 grams) of gold.

Valence and Equivalent Weights. An examination of the accepted formulas for copper chloride and gold chloride in comparison with that for hydrogen chloride will reveal an

interesting relationship. These are:

Hydrogen chloride **HCl** Copper chloride CuCl₂ Gold chloride AuCl₃

By inspection, one can see that the valence number of Cu is two and of Au is three. It will be recalled that the combining capacity of hydrogen is taken as unity and is the standard of comparison. The number of hydrogen atoms with which an atom of an element may combine, or which an atom of an element may displace from its compounds, is the combining number, or valence, of the element. We may also say that the weight of an element which is chemically equivalent to one gram-atomic weight of hydrogen shall be called its equivalent weight. Thus from the formula of silver chloride (AgCl) we may see that the valence number of silver is one, and that the equivalent weight of silver is the same as its atomic weight. To make this more clear let us compare this formula with that of hydrogen chloride (HCl). It may be seen that one silver atom combines with the same amount of chlorine as does one hydrogen atom. Thus, silver atoms have the same combining

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capacity as hydrogen atoms, and one silver atom is chemically equivalent to one hydrogen atom. From this it is evident that the equivalent weight of silver is the atomic weight (107.88 grams). Similar reasoning shows that the equivalent weight of copper in $CuCl_2$ is one half the atomic weight of copper or $\frac{1}{2}$ of 63.47 and that the equivalent weight of gold in $AuCl_3$ is one third of the atomic weight of gold or $\frac{1}{3}$ of 197.2.

By now it is evident that there is a relationship between the valence of an element and the amount of electricity which is required to set free a gram-atomic weight of it. Elements exist as ions in solutions from which they may be set free by simple electrolysis. The following table, which shows the relationship between the ionic charge and the electricity required for deposition of a few of them, may be helpful.

Ions	Valence	Coulombs of Electricity to release 1 atomic weight	Coulombs of Electricity to release 1 equivalent weight			
H^{+}	I	1 × 96,500	96,500			
Ag ⁺	I	1 × 96,500	96,500			
Cu++	2	2 × 96,500	96,500 96,500			
Au+++	3	3 × 96,500				

Thus there is a definite amount of electrical energy required to convert an equivalent weight of an ion to an equivalent weight of the free element. The amount of silver plate on a spoon may be measured by the amount of electricity required to put it there. In other words, there is a definite amount of electricity connected with the unit charge on an ion. And the total electrical charge connected with an ion is a multiple of this unit charge. It seems, then, that electricity must come in small units and that we must take a whole unit or nothing.

Faraday's Laws. Much of the foregoing evidence was investigated by Faraday. He summed up the information at hand in the two laws of electrolysis which bear his name.

1. The quantity of material set free at the electrodes is pro-

portional to the total amount of current which passes through the solution.

2. The same amounts of electricity will liberate weights of various elements which are proportional to their equivalent weights.

The quantity of electricity (96,500 coulombs) which liberates one equivalent weight of an element from its solution is called a faraday.

While this discussion has centered around metallic ions which bear a positive charge, it is not intended to infer that negative ions do not also undergo changes during the passage of electricity through solutions. They do. Thus while one equivalent weight of copper is deposited from a solution of copper chloride there is also one equivalent weight of chlorine liberated at the positive electrode.

Chemical Changes Are Electrical Processes. Since it has been shown that a definite amount of electricity is required to convert an ion to the free atom, it naturally follows that a definite amount of electricity left the atom at the time it became an ion. From what has gone before we should be able to write the reaction between chlorine and copper as a combination of the following changes.

$$Cu \rightarrow Cu^{++} + 2 \times 96,500$$
 coulombs $Cl_2 \rightarrow 2 \times 96,500$ coulombs $+ 2Cl^-$

In the light of this reasoning such chemical reactions involve a transfer of electricity from one atom to another. The question then arises as to what happens when such a transfer occurs and how it is possible. We may also ask if all elements behave alike in this respect and if any differences have been tabulated. In the above equations we assumed that copper gave up electricity to chlorine during their reaction together. But no reason for such an assumption was given.

THE CLASSIFICATION OF THE ELEMENTS

Newlands' Law of Octaves. So far as we are concerned the whole business of finding similarities between elements began back in 1865 when an Englishman, by the name of Newlands, presented a paper before an English scientific society. He proposed that certain elements known at that time could be arranged in the order of increasing atomic weights and that every eighth element would show similar characteristics. A few of these elements so listed will make this more clear. The figures represent the atomic weights.

1	7	9	11	12	14	16
H	Li	Be	В	C	N	O
F	Na	Mg	Al	Si	P	S
19	23	$2\overline{4}$	27	28	31	32

According to Newlands, certain similar characteristics are shown by each element of the pairs listed. Thus lithium (Li) and sodium (Na) are very much alike, as are also carbon and silicon, nitrogen and phosphorus, and oxygen and sulfur. This statement of similarity of every eighth element was called the law of octaves. It is interesting that a noted gentleman arose in the scientific meeting and asked Mr. Newlands if he had tried arranging the elements alphabetically. "Such an arrangement," he laughingly remarked, "would surely show some interesting things." This silly and sarcastic thrust drowned any enthusiasm which Newlands or other members of the society may have had.

Periodic Table of Mendeleeff. About 1869, a Russian by the name of Mendeleeff rediscovered the same idea. However, Mendeleeff took the idea much further and made greater use of the relationships which he found to exist. He claimed that the properties of the elements are recurring functions of their atomic weights. By this he meant that, as one lists the elements in the order of increasing atomic weights, it is found that the chemical properties encountered seem to go through periodic changes. He listed the then known elements in the order of

THE PERIODIC TABLE (Based on the classification of Mendeléeff)

						28 Ni 58.69		46 Pd 1 106.7		78 Pt 1 195.23				67 Ho 163.5	
(рамет он тие стамителион от лученцевен) Стопр		VIII				26 27 Fe Co 55.84 58.94		44 45 Ru Rh 101.7 102.91		76 77 Os Ir 190.2 193.1				66 Dy 162.46	
		VII		9 F 19.00	17 C1 35.457		35 Br 79.916	Ma 43 10	53 I 126.92		85			65 Tb 159.2	
		IN		8 O 00.01	16 S 32.064	Cr 52.01	34 Se 78.96	Mo 96.95	52 Te 127.61	W W 183.92	84 Po 210	U 92 238.07		64 Gd 156.9	71 Lu 175.0
		Λ		7 N 14.008	15 P 30.98	V 23 50.95	33 74.91	Cb 92.91	51 Sb 121.76	Ta 180.88	83 Bi 209.00	Pa 231?	ths	63 Eu 152.0	70 Xb 173.04
	Group	IV		6 C 12.01	14 Si 28.06	Ti 47.90	32 Ge 72.60	Zr 91.22	50 Sn 118.70	Hf 178.6	82 Pb 207.21	90 Th 232.12	The Rare Earths	62 Sm 150.43	69 Tm 169.4
		III		5 B 10.82	13 A1 26.97	Sc 45.10	31 Ga 69.72	39 Y 88.92	49 In 114.76	S7-71 Rare Earths	81 T1 204.39	89 230?		1 11 27 27	68 Er 167.2
		II		4 Be 9.02	12 Mg 24.32	20 Ca 40.08	30 Zn 65.38	38 Sr 87.63	48 Cd 112.41	Ba 137.36	80 Hg 200.61	88 Ra 226.05		59 60 Pr Nd 140.92 144.27	
		I	1 H 1.008	3 Li 6.940	11 Na 22.997	19 K 39.096	29 Cu 63.57	37 Rb 85.48	47 Ag 107.880	55 Cs 132.91	79 Au 197.2	87		58 Ce P 140.13 140	
		0		2 He 4.003	10 Ne 20.2	18 A 39.94		36 Kr 83.7		54 Xe 131.3		86 Rn 222		57 La 138.92	
			-	2	8	4	r.	9	1-	00	6	10			

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their increasing atomic weights. He then placed those elements with similar properties in the same vertical columns. In this respect his classification was like that of Newlands, and, like Newlands also, he had seven groups of elements. As the listing of the elements took place he soon discovered that certain elements did not fit the group where they seemed to fall but did fit the next group farther on. He then put these elements where their chemical properties indicated they should be even if it left blank places in his table. Three such blank spaces were obvious and he predicted the ultimate discovery of the elements which belonged in them.

At the time Mendeleeff outlined this classification, the elements, scandium, gallium, and germanium, had not been discovered. It was the spaces which these now occupy that he left blank. He not only lived to see the discovery of these elements, but they were found to have atomic weights and chemical properties in accordance with his predictions. There were still other elements unknown at that time. But he did not have information enough to draw conclusions concerning them. It is interesting to note that all of the rare gases of the atmosphere belong in a group together and that their discovery, soon after 1890, merely caused the addition of an entirely new column at one side of the table. Since these gases take part in no chemical changes and no compounds of them are known it is quite appropriate that this group be called group zero.

Irregularities of the Table. In keeping with his plan of putting each element where it seemed to belong, Mendeleeff left the three elements which follow manganese in a column to themselves. He realized that they did not fit anywhere else, and so he created an eighth group. Just what this meant, or how it could be explained, he did not know. But it is interesting that two more sets of three elements each are found farther down in this same group. He realized, too, that within the groups which he had created there were certain irregularities and that it was necessary to divide each group into two subgroups which he called families. The two families in each of the seven groups were alike in valence, but there were few other simi-

larities. Within each family, however, the similarity was quite striking.

There are fifteen elements, called the rare earths, which are very similar to each other. They follow barium in atomic weight. There was no way to spread these across the table since they all have the same valence and all seem to belong in group three. This being the case they have all been placed in this group. It has remained for later investigators to explain their peculiarity. Usually these elements are listed at the bottom of the table in order to save space in printing.

In spite of the fact that the order of increasing atomic

In spite of the fact that the order of increasing atomic weights dictates otherwise, there are three pairs of elements which have been placed in reverse order. These are argon and potassium, tellurium and iodine, and cobalt and nickel. There is nothing about the properties of any of these elements to indicate that they have been placed in the improper order. It would have been quite improper to have placed potassium, which is a very reactive metal, in group zero along with the inert rare gases.

The greatest single irregularity of the table is the fact that there is no place for hydrogen. Some workers place this element at the top of group seven while others feel that it belongs in the first group along with lithium and sodium. There are some good arguments for both of the views but there are also serious objections to them.

Uses of the Table. The periodic table, as arranged first by Mendeleeff, has been modified in certain respects. But the original idea remains intact. The existence of the table has stimulated considerable study of the elements, and this study, in turn, has much simplified the science of chemistry. Those elements which seem to be out of place have, of course, caused more than usual curiosity among chemists who want to find out what is wrong. They, therefore, have been studied with more than average intensity. The entire system of atomic weights has been checked and rechecked by many chemists, and many errors have been eliminated. For every peculiar thing in the table, there have been performed countless experi-

ments designed to prove or disprove the facts which were known at the time the table was arranged. The vacancies in the table provoked the research which brought forth the discovery of the missing elements. There were several vacancies among the elements of higher atomic weights and all of these have been filled, with the possible exception of two or three about which there is still some question.

The peculiar arrangement of group eight, and the long list of rare earths which appear together in group three, have been the centers of many investigations. Even though there are many things about these and other points of the periodic table which have not been explained yet, there are untold new facts which have been brought to light. It is these facts which add to our storehouse of knowledge and without knowledge progress is impossible.

It is not to be implied that the periodic table can ever be defended against all objections. It is now known that the properties of the elements are not determined by their atomic weights, but the table still remains. It is also known that most of the elements as we know them are mixtures of atoms with different atomic weights (you have heard of heavy hydrogen). All the atoms of any one element, however, have the same chemical properties. The atomic weights of the elements as listed are really the averages of these differently weighted atoms as determined by their relative abundance in nature.

There are certain advantages in using the periodic table which soon become apparent even to the layman or beginner in chemistry. Instead of remembering thousands of facts about the ninety-two elements, we can order these facts into nine groups. There are many properties of the elements which may be predicted from the position which they occupy in the table. If we omit the zero group and draw a line from the upper lefthand corner to the lower right-hand corner of the table, it will just about separate the metals from the nonmetals. Those elements in group eight and certain others are exceptions to this. But all of those elements which are to the left of such a line are among the metals. Those elements which fall near the

line, so drawn, are neither strongly metallic nor strongly nonmetallic and many of them show some properties of each class.

The most reactive nonmetal is fluorine which is found in the upper right of the table. The most reactive metal known is cesium, which is found at the lower left, though element number 87 should be still more reactive if it ever is obtained in sufficient quantity. Those elements which appear near to these two are also quite reactive, but this reactivity grows less with those which are farther away.

Those elements which occur in the same group all have the same combining number or valence. Those in group zero have a valence of zero; those in group one have a valence of one; those in group two have a valence of two; those in group three have a valence of three; and those in group four have a valence of four. In the groups higher than four, there are two or more common valences. Thus elements in group five show a valence of three toward hydrogen, but show valences of three or five when combined with oxygen. Those elements in group six have a valence of two when combined with hydrogen, but have valences of four or six when combined with oxygen. Those elements of group seven have a valence of one when combined with hydrogen, but have valences of one, three, five, or seven when combined with oxygen. The elements of group eight have valences of two or three. Such knowledge as this is easily classified and permits the finding of valence very readily.

The Atoms Are Related. As we examine the table by passing from left to right along a horizontal row (series), we soon discover that the properties of each succeeding element are slightly changed from those of the one which came before. It is also observed that a very reactive nonmetal occurs just before a completely inert gas, and that a very reactive metal occurs just after the inert gas. We can hardly fail to see, then, that some relationship other than an accidental one must exist. Something seems to have been added to each element in turn until a stable condition is attained in an inert gas. After this, the next addition of whatever it is which is added causes the for-

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mation of another active metal. We are at once faced with the fact that something smaller than the atom must exist, and that it is this smaller particle which determines the properties of the elements.

SUMMARY

The volt is the unit of electrical pressure.

The coulomb is the unit of electrical quantity.

The ampere is the unit of rate of electrical flow equal to one coulomb per second.

The ohm is the unit of electrical resistance within a conductor.

The electrical charge borne by an ion appears to impart special properties to the particle so charged. The ions of elements no longer have the properties usually associated with the free element. This electrical charge must come into evidence during the chemical reaction between elements.

Sir Humphrey Davy discovered sodium, potassium, barium, calcium, strontium, and magnesium by passing electricity

through the melted oxides of these elements.

Michael Faraday made the first serious study of the amount of electricity connected with an atomic weight of an element when in solution as a compound. He discovered an exact relationship between an equivalent weight of an element and the amount of electricity required to liberate it from its compounds. Faraday's laws state that the quantity of material set free at the electrodes is proportional to the total amount of electricity which passes through the solution, and the same amounts of electricity will liberate chemically equivalent amounts of the different elements.

The relationships and similarities between elements were studied by Newlands who proposed a law of octaves. Later, Mendeleeff proposed the periodic table in which he assumed that the properties of the elements are recurring functions of their atomic weights. He was able to predict the existence of certain undiscovered elements and he specified what their

properties would be. Their later discovery showed that in this he was exceedingly correct.

In the construction of the periodic table, Mendeleeff used the method of common sense in that he let reason dictate the position given to elements even if this was sometimes contrary to the general idea which he proposed. Any irregularities were left for further investigation and possible explanation at a later time.

The greatest irregularities in the periodic table are: the lack of complete similarity between the two families within a group; the existence of the misfit elements in group 8; the inverted order of argon and potassium, tellurium and iodine, and cobalt and nickel; the existence of the rare earths in one group; and the lack of a position for hydrogen.

The table is useful in that it stimulated research to explain the irregularities; allows a classification of the knowledge of elements into a few general classes; and serves as an easy way to obtain valence numbers. It also impresses us with the interrelationships between elements.

REVIEW QUESTIONS

- 1. Write equations in ionic form to show the union of NaOH with HCl.
- 2. Cite some differences between the sodium atom and the sodium ion; between the chlorine atom and the chloride ion.
- 3. What names are given to the units of electrical pressure, quantity, rate, resistance?
 - 4. Who discovered sodium? By what method was it obtained?
- 5. Who first studied the effect of electricity on solutions of electrolytes?
 - 6. State Faraday's laws.
- 7. What quantity of electricity is required to deposit an atomic weight of silver from a solution of silver nitrate?
- 8. What was the basis of Newlands' classification of the elements?
- 9. What was the basis of the classification of the elements by Mendeleeff?

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10. What should be the formula of a compound containing only phosphorus and hydrogen? Phosphorus and oxygen?

11. What are the combining numbers of the elements in the

various groups toward hydrogen? Toward oxygen?

12. List the irregularities of the periodic table.

13. State some of the advantages of the periodic table.

14. In what position in the periodic table do you find the active

metals? Where do you find the active nonmetals?

15. What is the chief chemical property of the elements in group zero?

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CLASSIFICATION OF THE ELEMENTS, CONTINUED. MODERN ATOMIC THEORY. RADIOACTIVITY

The Electrical Nature of Matter. The facts which have been presented leave little doubt but that there is some sort of relationship between the chemical activity of an element and its electrical condition. We have seen that the amount of electricity required to deposit an atomic weight of an element from its solution is proportional to the electrical charge on the ions of the element. And we have observed that equal quantities of electricity will deposit chemically equivalent quantities of the various elements from their solutions. It is also clear that the valence (combining number) of an element is the same as the electrical charge of the ions of the elements. It then follows that the electrical charge which an element may have in solution is related to the position of that element in the periodic table.

The ions of certain elements (such as sodium, calcium, potassium, and other metals) are charged with positive electricity as is shown by the fact that they are attracted to the negatively charged electrode during electrolysis. On the other hand such elements as fluorine, chlorine, sulfur, and other nonmetals give ions which are charged with negative electricity. Other elements such as carbon and nitrogen do not seem to form simple ions, and a look at the periodic table will show that these are about midway between the metals and nonmetals in a horizontal row.

We may summarize these facts by reference to the periodic table again. If we follow the order of the elements in the table from left to right, we find that the elements which come after

the inert rare gases give positive ions in solution and that the elements which come just before the inert rare gases give negative ions in solution. The elements in between these two extremes are more or less "on the fence," and many of them give no simple ions in solution.

The Nature of the Charge. Something of the nature of this charge may be learned from a study of electrical discharges in a partially evacuated tube. If a high voltage current is applied

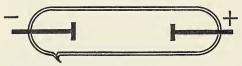


Fig. 34. Vacuum Discharge Tube

to two electrodes contained in a partially evacuated tube similar to the sketch in Figure 34 a current will flow. Investigation has

shown that very small particles leave the negative electrode and strike the positive electrode. Very exact experiments have determined the mass of these particles and it is found to be about 1/1845 that of the hydrogen atom. Other experiments have shown that each of these particles bears a definite electrical charge and that it is always the same regardless of the metal of which the electrode may be made and regardless of the kind of gas in the tube. When the particles so generated strike the positive electrode they give rise to very short light waves which are called x-rays. It is upon this principle that x-ray tubes are built. It has also been observed that metal wires, heated to a bright heat, emit particles which bear electrical charges just like the charge on the particles in the evacuated tube. Also, if x-rays are allowed to strike a metal surface these same negatively charged particles are emitted from the metal. Further investigation has shown that exactly the same kind of charged particles are emitted from radium because of its spontaneous decomposition.

Because of this similarity between the particles which may be produced by so many different methods, it has been assumed that these particles constitute the "units" of electricity. The name "electron" has been proposed for them and it has been universally accepted.

If we refer again to the experiment with the partially evacuated tube, we find that electrons are not the only charged particles encountered. Some carefully controlled experiments have shown that other particles are streaming toward the negative electrode. These particles are charged positively, and their size depends upon the gas which remains in the tube. When this gas is hydrogen the particles have the mass of the hydrogen atom, and the positive charge is exactly equal in magnitude to the negative charge of the electron. In case another gas is present in the tube these particles have the mass of the atoms concerned, and each bears one or more units of positive charge. Thus it seems that the positive charges are bound up with the atoms of the elements and are not free to appear alone as do the electrons. No cases are known in which a unit positive charge is thus produced on any particle of less mass than the hydrogen atom. The positively charged hydrogen atom is called the proton. There is strong evidence to support the view that it is a hydrogen atom which has been stripped of an electron.

Atomic Numbers. A young English physicist, Henry G. J. Moseley, who was killed at Gallipoli in 1915 at the age of 27, studied the behavior of the solid elements when they were bombarded by streams of electrons. We have pointed out that this bombardment causes the production of x-rays. Moseley measured the wave length of the x-rays so produced and arranged the elements in the order of increasing frequency of the x-ray emitted. This order was found to be the same as that already given in the periodic table. Moseley assigned an atomic number to each element in order to indicate the position of the element in the series which he arranged. These atomic numbers are usually given in all tables of atomic weights as well as in various arrangements of the periodic table. This order as determined by Moseley is the same as the order of increasing atomic weights, except in the cases that we pointed out in our discussion of the periodic table. In the original table, argon and potassium, cobalt and nickel, and tellurium and iodine, are pairs of elements which appear in reverse order to that of their atomic weights. The series which Moseley prepared placed these elements in their proper order. It is believed that the frequency of the emitted x-rays depends upon the arrangement of the electrons which are in the atoms as well as upon the number of protons and electrons which may be present.

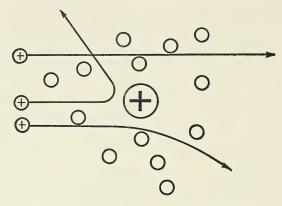
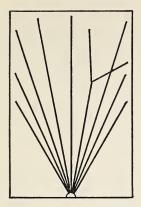


Fig. 35. Deflection of Alpha Particles Passing Through an Atom

Rutherford's Contribution. Something of how the atom is constructed was demonstrated by Rutherford, an English physicist. When radium decomposes it gives off charged particles, called alpha particles, which have an atomic weight of four and which bear a positive charge equal to that on two protons. These alpha particles are emitted with rather high velocities. They are capable of passing through thin metallic sheets with very little deflection, that is, without being thrown a little aside from a straight course. Rutherford studied the penetration of metallic sheets by these particles and measured the deflections. A few of the alpha particles used were found to be thrown considerably out of line and in some cases they emerged from the metal on the same side from which they entered. This is illustrated in Figure 35. He pointed out that the metallic atoms must be porous except for a very small part of their volume and that when an occasional alpha particle struck this nonporous part of the atom it was greatly deflected. Rutherford proposed that the atom is made up of a



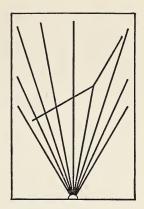


Fig. 36. Diagram of Fog Tracks

very small but quite dense nucleus surrounded by electrons and that it was the nucleus which produced the deflections of the alpha particles. He calculated the units of charge on the nucleus from the deflections of the alpha particles and found that this was always equal to the atomic number. Rutherford then proposed that the nucleus contains all of the protons and a part of the electrons packed very close together and that the remaining electrons occupy space surrounding the nucleus in a somewhat porous structure.

Path of Alpha Particles Through Air. An experiment was devised by C. T. R. Wilson which shows the path of alpha particles through air. A small amount of radium is enclosed in air supersaturated with water vapor. The alpha particles from the radium pass through the air molecules and jar loose some electrons from the atoms. Thus they leave a path strewn with positively charged atoms and these attract water molecules to produce stringlike patches of fog known as fog tracks. Most of these are straight lines from five to seven centimeters in length. But once in a great while one is seen which shows a great deflection as if the alpha particle had struck a solid wall. This deflection is due to a direct hit on a nucleus. About 130,000 air molecules are passed through by each alpha particle, and so the nucleus must be quite small or it would be banged into much more often.

Planetary Electrons. This common conception of the atom, which is now accepted, pictures all of the protons and some of the electrons in the nucleus. The positively charged nucleus which is so formed is balanced electrically by the remainder of the electrons which move around the nucleus in some way such as the planets move around the sun. These are called planetary electrons. Since the charge on the nucleus is the same as the atomic number there must also be this same number of planetary electrons.

The Hydrogen Atom. Hydrogen is the lightest element known and has the atomic number of one. It thus has a single positive charge on the nucleus and has a single planetary electron moving about it. Since the atomic weight is the same as that of the proton we assume that its nucleus is surely a single proton. It has been calculated that the radius of the hydrogen atom is about 10-8 cm. (1/100,000,000 cm.) and that the radius of the electron is about 2×10^{-13} cm. (2/10,000,000,000,000)cm.) or about 1/50,000 that of the entire atom. The proton however is only about one one-hundred-millionth as great in radius as is the atom. Thus it would appear that most of the space occupied by the atom must be empty and devoid of matter entirely. If things in general are so made up it is clear that there is little solid matter in anything, and that things like the steel body of an automobile, or a granite rock are much like a sponge with far more empty space than material.

The Helium Atom. Helium has an atomic number of two and an atomic weight of four. This means that the nucleus must contain four protons in order to make up the weight and yet must have only two positive charges. If two electrons also exist in the helium nucleus the matter of the nuclear charge will be cared for. To complete the atom there must be two planetary electrons revolving about the nucleus.

The Neutron. Within the past few years it has been definitely shown that there is an uncharged particle with a weight nearly the same as the proton. It is produced when certain elements, such as beryllium, are bombarded with alpha particles. This has given rise to the idea that the nuclei of all atoms are

composed of neutrons and protons instead of protons and electrons. In such case, the number of protons in the nucleus is equal to the atomic number and the number of neutrons is sufficient to account for the remainder of the atomic weight. It follows from this that the number of planetary electrons is the same as the number of protons in the nucleus.

Arrangement of Planetary Electrons. For many years there have been several questions concerning the arrangement of the planetary electrons within an atom. It is fairly well agreed, among both physicists and chemists, that these electrons must be in rapid motion. But it is impossible to see them and therefore their exact arrangement may be determined only by working it out theoretically together with ingenious experiments. We have already mentioned that the number of planetary electrons is the same as the atomic number. Thus as we encounter the heavier atoms we must have to do with an everincreasing number of these electrons. It has been fairly well established that these electrons are probably arranged about the nucleus in a series of concentric orbits. These orbits probably follow paths contained in the surface of a sphere, or perhaps in the surface of a thing shaped like a football. Thus in the case of hydrogen, which has a single electron moving about a single proton, we assume that the electron normally remains in what we shall term the first sphere, or shell. The second element, helium, with two planetary electrons is completely inert (chemically inactive) and we assume that the second electron is in the same shell with the first. These are drawn diagrammatically as follows:

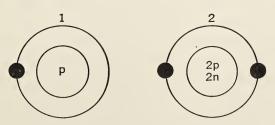


Fig. 37. Structure of the Atoms. Hydrogen and Helium

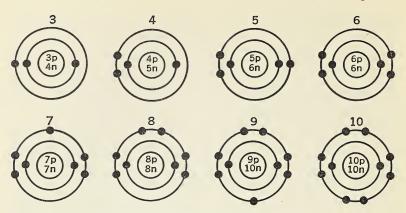


Fig. 38. Structure of the Atoms. Lithium to Neon

The third element, lithium, has rather great chemical activity. We assume that its third electron must be in a second, outer, shell. This may be expected to produce an atom in which the outer electron is relatively far away. It should, then, easily lose this electron to produce the positive lithium ion. The fourth element, beryllium, must have four planetary electrons, of which two are in the first shell, and two more are in the second shell. Thus this element may lose two electrons to produce the ion having two positive charges. Boron is the fifth element and outside its nucleus there are five electrons, three of which are in the second shell. In a like manner the sixth element, carbon, has four electrons in the second shell; nitrogen, the seventh element, has five electrons in the second shell; oxygen, the eighth element, has six electrons in the second shell; and fluorine, the ninth element, has seven electrons in the second shell. The next, or tenth, element, neon, must have eight electrons in the second shell, and here again we find a completely inert gas. It must be that when the second shell of electrons contains eight it is full and quite stable.

The diagram of each of these atoms is shown in Figure 38. Element number eleven is sodium and here again we find an element which possesses great reactivity. It easily loses one electron to form the positive sodium ion and thus we assume that this single electron is in a shell still farther away than

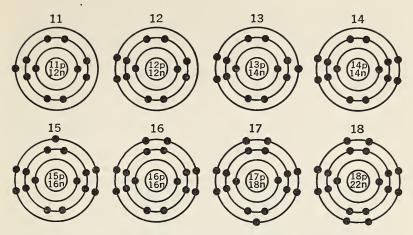


Fig. 39. Structure of the Atoms. Sodium to Argon

the second shell. The atoms of the elements next in order are pictured as being built up in a way similar to that described above. Each succeeding element has one additional electron and this is placed in the third shell. When the eighteenth element has been reached this third shell contains eight electrons also and we find this element to be another inert gas which is argon. Figure 39 shows these atoms.

Chemical Combinations. Let us refer to the elements whose structures have been pictured and consider each of them in the light of its valence. Those which come immediately after the inert gases tend to lose the electrons which are in the outer shell. This leaves the next lower shell exposed and this represents a stable or inert condition. Thus sodium is extremely active chemically and decomposes water with great rapidity. After losing its single outer electron, however, it becomes inert in the form of the sodium ion. Magnesium burns in the air to give a brilliant white light, but in the form of its compounds it is not combustible. The two outer electrons have been lost during the process of chemical combination.

On the other hand let us consider fluorine and chlorine. These two elements represent the most active nonmetallic elements. Both of them are highly poisonous and attack most metals with great rapidity. However, in the form of their salts

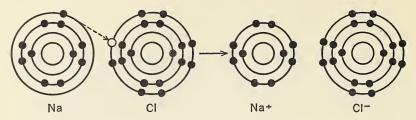


Fig. 40. Reaction of Sodium with Chlorine to Form Sodium Chloride

they lose both of these properties to a considerable degree. We notice that each of these elements possesses atoms which lack a single electron to give them an outer shell of eight electrons. It seems that this makes them so reactive and that as soon as they gain this electron from something else they are entirely satisfied.

Let us picture the formation of common salt, sodium chloride, from the elements sodium and chlorine. It has been pointed out that sodium is more stable after losing an electron, and chlorine is more stable after gaining an electron. By bringing these two elements together it should be possible to satisfy each of them. What probably happens is pictured in Figure 40. The resulting substance, sodium chloride, dissolves in water to give sodium ions which bear a single positive charge and chlorine ions which bear a single negative charge. The ions are completely inert and thus we feel safe in assuming that each of the atoms now possesses a stable arrangement of the electrons. This explanation begins to shed light upon the question of chemical combination which was raised earlier when it was suggested that some relationship must exist between electricity and chemical combination.

Valence. When a reaction takes place between sodium and chlorine it involves a single electron. Thus we may say that each of these elements has a valence of one. This is in complete agreement with our discussion of the periodic table. If magnesium reacts with chlorine, we see that one magnesium atom may furnish two electrons, and, since one chlorine may accept only one electron, it requires two chlorine atoms for each

magnesium. Thus it follows that magnesium has a valence of two. Such valences in which an electron leaves one atom and goes to another are called polar or electrovalences.

Certain of the elements may combine without the complete transfer of an electron. It seems that the attractive forces are not enough to tear the electrons away from either of the reacting elements and as a result they each share a number of

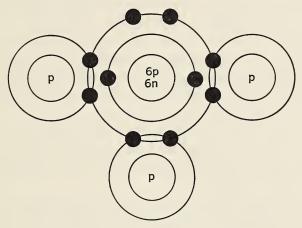


Fig. 41. Structure of the Ammonia Molecule

electrons. Hydrogen and nitrogen can be made to react to form the gas called ammonia (NH₃). After the reaction the two elements do not exist as charged ions but remain together as the complete molecule of the new compound. We assume that this represents a case where each atom has a stable condition of the electrons by sharing them rather than by a transfer of them. This compound may be represented by Figure 41. The resulting compound contains a nitrogen atom which has eight electrons in the outer shell and contains hydrogen atoms which have two electrons in their outer shell. It may be remembered that in the case of helium two electrons in this shell next to the nucleus represents a stable condition. Thus by sharing electrons all of the atoms possess a stable structure. Valences of this type in which electrons are shared are called nonpolar or covalences. This type of valence is encountered

with those elements of groups 3, 4, and 5 which lie in between the two extremes of expulsion and attraction of electrons.

We may summarize the above discussion of valence with a

few generalizations.

1. Those elements whose atoms contain less than four electrons in the outside shell (the metals) tend to give up these electrons to the nonmetal with which they react so that the next lower shell which resembles an inert gas will be exposed. As a rule this results in a polar valence.

2. Those elements whose atoms contain more than four electrons in the outside shell (the nonmetals) tend to take up electrons from the metals with which they react so that they will complete their outside shell of eight electrons and

thus resemble the next higher inert gas.

3. Those elements whose atoms contain three to five electrons in the outer shell tend to complete their outer shells by sharing electrons with another element. As a rule this results in a nonpolar valence.

4. The numerical value of a polar valence shown by an atom is the same as the number of electrons which that atom may give up to another atom or take from another atom.

5. The numerical value of a nonpolar valence shown by an atom is the same as the number of electrons which the atom

contributes to the sharing process.

Isotopes. From the theory of atomic structure it follows that the chemical behavior of an element depends almost entirely upon the number of electrons in the outer electron shell. If one considers the elements from this point of view it makes but little difference what the weight of the nucleus is or what may be in it. Thus it should be possible to have two atoms with an identical number of electrons outside the nucleus and an identical number of electrons in the outer shell and yet have their nuclei of different weights. Such atoms should have identical chemical properties. An example of this is found in the atoms of chlorine. It has been definitely shown that two weights of chlorine atoms exist and that ordinary chlorine is a mixture of these two kinds of atoms. The average atomic

weight is 35.46 as shown in the tables. Diagrams of the proposed structure for these differently weighted atoms are shown in Figure 42. Atoms with different weights but with identical electron structures are called isotopes. A great many elements have been shown to have two or more isotopes and it is mixtures of these which occur in nature and which have been used to determine atomic weights. Strangely enough it seems that

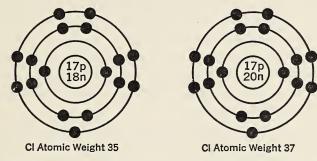


Fig. 42. There are Two Weights of Chlorine Atoms

wherever these elements are found in nature they occur as the same mixture of isotopes and thus constant values are obtained for their atomic weights.

Most of us have read something of heavy hydrogen (called deuterium for convenience) and the water which contains atoms of this heavy isotope of hydrogen. As found in nature, one atom out of every 5000 atoms of hydrogen has an atomic weight which is twice that of ordinary hydrogen. These are chemically almost identical.

RADIOACTIVITY

In 1896, Becquerel, a French engineer and physicist, discovered that uranium compounds give off something which affects a photographic plate. Madame Marie Curie and her husband, Professor Pierre Curie, began to investigate the ores of uranium and they found other substances which were even more active toward a photographic plate than is uranium. They discovered the elements *polonium* and *radium*.

Soon after the discovery of radium it was observed to produce three different things *spontaneously*. Two of these appeared to consist of electrically charged particles with definite masses. By means of magnetic fields and electrically charged plates these two kinds of particles were separated. One of them was helium. These particles were at first charged like ions and may be represented as He⁺⁺. Such particles which are given off from radium are called *alpha particles*. These are literally blown out of radium at a speed of about 20,000 miles per second. They hit so many molecules in the air, as soon as they leave the radium, that they travel only about eight centimeters before being stopped completely. Somewhere along this path they pick up two electrons, which is all they need to become ordinary atoms of helium.

Another kind of particle emitted from radium is found to have a charge of negative electricity. These became known as *beta particles* and are now proved to be electrons. Some of these travel as fast as 180,000 miles per second which is almost the speed of light. These are moving so fast that it takes more to stop them than it does for the alpha particle. They may pass through one centimeter of water, or one millimeter of lead before coming to rest, or at least before they lose their individual force.

The third thing produced by the spontaneous decomposition of radium has been called the *gamma* ray. This has been shown to consist of very short x-rays. Since x-rays are not charged with electricity they are not affected by a magnet.

This spontaneous decomposition of radium is similar to a decomposition which takes place with a number of other elements such as uranium, thorium, polonium, and actinium. Each of these decomposes with the production of alpha particles, electrons, and short x-rays. The process has come to be known as *radioactivity*. Attempts to slow it down or to speed it up have failed. Studies made have shown that after a bit of radium decomposes it no longer is radium. The particles which come off of radium are the results of explosions of the atomic nucleus. A definite part of the nucleus leaves. This part,

in the case of radium, is the charged helium atom and the part which remains behind is the gas called *radon*. This is an element in the zero group of the periodic table. Radium decomposes very slowly as first one and then another atom "blows up." In about 1700 years any given amount of radium will be half gone. It will then take another 1700 years for half of the remainder to decompose.

From radon we find a series of substances, each produced from another by decomposition which at the same time liberates an alpha particle or an electron. Finally, a form of lead results and the decomposition ceases. It has been established that radium results from the decomposition of uranium through another series of decomposing substances. In all, there are some thirteen different radioactive elements which are formed after uranium decomposes and before the end product, lead, is produced.

Transmutations. The old idea of the alchemist was to produce gold from lead and other less expensive elements. So violent was the reaction against the fraud of the alchemist that even the thought of transmutation fell into the discard along with the alchemist himself. It was impossible; why think of it? In radium and the other radioactive elements we see conclusive evidence that one element may change into another. In order that this may be done it is necessary that something happen to the nucleus of the atom. In all of the spontaneous changes which have been mentioned the nucleus explodes and ejects electrically charged particles. The reversal of this process has been thought possible.

If an electrically charged particle could be forced to strike the nucleus of an atom it could possibly "fuse" with the nucleus and thus produce a new atom. Such an atom could have different chemical properties from the old atom. The thing to do would be to shoot charged particles at the nucleus of an atom and see what happens. It must be remembered, however, that shooting at a nucleus is one thing and hitting it is another. The nucleus occupies such a minute part of the total volume of the atom that only one out of possibly millions of "bullets" could score a direct hit. The best of scientists have long considered this possibility as worth trying.

Rutherford succeeded in bombarding nitrogen atoms with alpha particles some twenty years ago. He obtained proof of the formation of a few protons. He imagined that these were shot out of the atom nuclei in much the same fashion as a small boy may shoot a marble out of a ring. Ten years later this work was repeated and it was shown that when the proton was removed from the nucleus there remained an isotope of oxygen with a mass of 17. We may write this in the form of an equation.

$${\rm He^4 + N^{14} \rightarrow O^{17} + H^1 + energy}$$

The superscript indicates the atomic weight of the atom concerned.

This discovery added new interest to the study of transmutation. Other "bullets" for piercing the atom were sought. Besides the alpha particles obtained from radioactive disintegration of various elements there are four available means for this. Electrons may be obtained from radioactive elements, from heated substances, and from vacuum tubes similar to x-ray tubes. Protons may be obtained from vacuum tubes containing a trace of hydrogen. When the current passes through the tube the protons stream toward the negative electrode and strike a thin metallic window which permits them to pass out of the tube. Neutrons are produced during the bombardment of beryllium and a few other elements by alpha particles. These neutrons are uncharged and hence may approach the positive nucleus of an atom without electrical repulsion. Deuterons are the nuclei of heavy hydrogen atoms. These may be produced in a fashion similar to that used to produce protons.

Atom Smashers. In order to give the atom-piercing particles all of the energy possible, Lawrence and his helpers at the University of California have devised what they call a cyclotron. This instrument employs a gigantic magnet which causes the "bullets" to travel in a circular path while they are given ever-increasing speeds by the oscillation of an electrical

field. When the particles attain energy corresponding to what they would have after falling through about 5,000,000 volts they are thrown out of the circular path and leave the magnetic field. If one of these particles hits an atomic nucleus it is apt to penetrate it and become indistinguishable from the rest of the nucleus.

As an example, let us consider the case of the bombardment of nitrogen atoms by rapidly moving neutrons as done by Harkins of the University of Chicago. The nucleus of the nitrogen atom with a mass of 14 is struck by a neutron with a mass of 1. These fuse together and a nitrogen atom with a mass of 15 (an isotope of ordinary nitrogen) results. Although nitrogen 15 isotopes exist in nature as stable atoms the nitrogen 15 isotopes formed by this method are unstable and explode to produce atoms of boron and atoms of belium.

$$N^{14}$$
 + n^1 \rightarrow N^{15} \rightarrow B^{11} + He^4

Induced Radioactivity. In 1934, Irene Curie, together with her husband, Frederic Joliot, reported the discovery that the elements boron, magnesium, and aluminum become radioactive after being bombarded with alpha particles. This radioactivity persists for some little time after the bombardment ceases. Fermi and his helpers in Italy carried this work further and showed that more than forty different elements may be made radioactive by bombardment with neutrons. This change with phosphorus is shown.

$$P^{31} + n^1 \rightarrow Al^{28} + He^4$$

The aluminum with mass 28 is unstable and it emits an electron from the nucleus.

$$Al^{28} \rightarrow Si^{28} + electron$$

This emission of an electron by the isotope of aluminum constitutes the radioactivity of this substance. It is quite similar to the change which occurs with some of the regular radioactive elements.

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An interesting possibility for the use of artificial radioactivity has been suggested. If common salt is bombarded with neutrons it produces atoms of radioactive sodium.

$$Na^{23} + n^1 \rightarrow Na^{24}$$

This isotope of sodium is radioactive and begins to decompose by ejecting an electron from the nucleus. Magnesium results.

$$Na^{24} \rightarrow Mg^{24} + electron$$

The emission of electrons by the bombarded salt rapidly decreases after about 15 hours. Since it is the electrons given off from radium which are desired in treating cancer it is possible to use radioactive sodium in place of radium for these treatments. The radiations from sodium would not continue for long periods of time and hence could not harm normal tissue as does radium.

This brief discussion of radioactivity and transmutation may give a little idea of what is going on in the field of nuclear physics and chemistry. The subject is much too vast to attempt further understanding at this time.

SUMMARY

The chemical properties of an element are closely related to the position of that element in the periodic table. The tendencies of elements to form ions as well as the charges of the ions are likewise related to this position.

Electrons flow from the negative electrode toward the positive electrode in evacuated tubes which are connected to a source of high voltage electricity. The same sort of electrons are emitted by hot metals, or by metals subjected to x-rays, and by radium. Electrons bear a charge of negative electricity.

Positively charged particles flow toward the negative electrode during the operation of a vacuum tube. These have masses which depend upon the gas which remains in the tube.

X-rays are produced when high-speed electrons strike a metal target. The wave length and frequency of these x-rays

is determined by the metal of which the target is composed. By arranging the elements in the order of the increasing frequency of the emitted x-rays, Moseley devised the system of atomic numbers. This follows the order used in the periodic table.

Rutherford calculated the charge on the nucleus of certain atoms by measuring the deflection of alpha particles as they passed through thin sheets of metals.

As alpha particles pass through air they bring about the ionization of many thousands of molecules. These ions serve as condensation points for moisture in saturated air. Under certain conditions each alpha particle leaves a string of fog to mark its path.

The modern concept of the atom suggests that practically all of the mass of an atom is concentrated in a small nucleus which is surrounded by planetary electrons. These electrons are assumed to move in special orbits. The chemical properties of an element depend upon the number and arrangement of these.

The nucleus is assumed to be composed of protons and neutrons. The number of protons is equal to the atomic number and to the number of external electrons.

Chemical combinations occur because of electron transfer between two elements or because of electron sharing between two elements. The combining number of an element is equal to the number of electrons transferred or to the number of electrons contributed to the sharing process. Electron transfer results in a polar or electrovalence. Electron sharing results in a nonpolar or covalence.

Elements which have atomic numbers just smaller than the rare gases tend to accept electrons, and elements with atomic numbers just larger than the rare gases tend to donate electrons during chemical union. Those elements in between these two extremes tend to form covalent linkages.

Two elements with the same atomic numbers have the same number of planetary electrons. The number of neutrons in their nuclei will differ. These elements will have different atomic weights but the same chemical properties. They are

called isotopes.

Radioactive elements decompose spontaneously with the emission of alpha particles, beta particles, and gamma rays. These are charged helium atoms, electrons, and x-rays respectively. There is a series of elements formed during ordinary radioactive decay.

High-speed particles such as alpha particles, electrons, neutrons, protons, and deuterons have been directed toward the atoms of elements. This has resulted in the transmutation of some of these into other elements. The new nucleus formed as a result of the collision appears to undergo a partial disintegration. This type of experimentation has led to induced radioactivity.

REVIEW QUESTIONS

1. For what reason do we assume the ions of the metallic elements to be charged positively?

2. What two types of particles are produced during an electrical discharge through a partially evacuated tube?

3. What gives rise to the production of x-rays in an x-ray tube?

- 4. What is the basis of the atomic numbers assigned by Moseley?
- 5. What led Rutherford to propose the nuclear idea of the atom?
- 6. Why are the electrons which surround the nucleus called planetary electrons?
 - 7. What are the relative sizes of protons, electrons, and atoms?
 - 8. What sort of particle does the neutron appear to be?
- 9. Draw diagrams to represent the atoms with atomic numbers from 1 to 10.
- 10. How does the idea of eight electrons in the outer shell of an atom seem to fit the facts brought out by the periodic table?
- 11. Describe the union of sodium and chlorine atoms in terms of our modern theory. Do the same for the union of magnesium and bromine atoms.
- 12. What name do we give the valence forces between the sodium and chlorine in a molecule of sodium chloride?

13. Describe the union of hydrogen and nitrogen atoms to form ammonia. What name do we give to these valence forces?

14. What do we mean by isotopes? What is the relationship of

their properties?

15. Try to formulate a definition of an element on the basis of the Dalton theory. Do this also in the light of our modern knowledge.

16. What happens to an atom when it undergoes radioactive

disintegration?

17. What is the nature of each of the three kinds of radiation emitted by the radioactive elements?

18. What are alpha and beta particles?

19. What may happen to an atom nucleus which is struck by a rapidly moving particle?

20. Why must we discard the idea that the transmutation of

elements is impossible?

21. Why may radioactive sodium become useful? How is it

prepared?

22. List some contribution made by each of the following people. Madame Curie, Rutherford, Becquerel, Fermi, Irene Curie, Joliot, Moseley.

23. Who discovered deuterium? What is its relation to hydrogen?

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SALT: PRODUCTS OF ELECTROLYSIS

We have seen (Chapter 14) that the passage of an electric current through a solution of a salt causes a deposit of elements at the electrodes. Thus, copper, gold, silver, and hydrogen as well as many other elements may be set free from their compounds in this manner. From the study of electronic structure it becomes apparent that the process of electrolysis involves the restoration of electrons to the positively charged ions and the removal of electrons from the negatively charged ions. If a solution contains more than one kind of positive ions it naturally follows that the one which most easily accepts electrons from the negative electrode will be the first to be released as the element. We may get some idea of this relative "affinity" for electrons if we recall the method for preparing hydrogen from acids by the addition of an active metal. If zinc is placed in a solution of hydrochloric acid the zinc gives up electrons to the hydrogen ions of the solution.

$$Zn + 2H^+ \rightarrow H_2 + Zn^{++}$$

From this we may conclude that hydrogen ions will combine with electrons more readily than will zinc ions.

If sodium is placed on water there is a rapid reaction which results in the evolution of hydrogen and the formation of sodium hydroxide in the solution. It is easy to account for this behavior since all water solutions contain hydrogen ions which will accept electrons if some source of electrons is available. Since sodium atoms give up electrons with relative ease, it is not surprising that they force the hydrogen ions to

accept electrons. Just as soon as a hydrogen ion gains an electron, it becomes a gas and must behave as such. The hydrogen ions are furnished by the water which ionizes.

$$H_2O \Leftrightarrow H^+ + OH^-$$

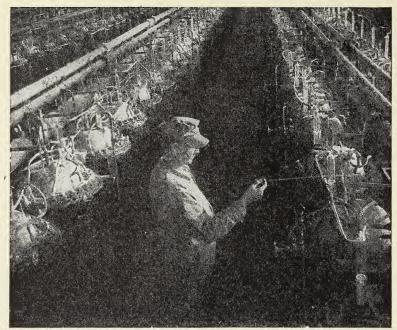
The OH⁻ ions which remain in solution after the release of some of the hydrogen ions cause the water to become quite alkaline since the sodium ions do not produce acids as do hydrogen ions. The reaction of sodium with water may be written as

$$\begin{array}{c} \mathrm{Na} \, + \, \mathrm{H}^{+} \, + \, \mathrm{OH}^{-} \rightarrow \mathrm{Na}^{+} \, + \, \mathrm{OH}^{-} \, + \, \mathrm{H} \\ 2\mathrm{H} \rightarrow \mathrm{H}_{2} \end{array}$$

As fast as the hydrogen ions are removed from solution more of them are formed by the ionization of more water molecules. Evaporation of the remaining water will leave solid sodium hydroxide.

Electrolysis of Salt. If a solution of sodium chloride is subjected to electrolysis, by means of carbon electrodes connected to an electric battery or to an electric generator, the products are those which we would expect. The battery, or generator, serves as an electron "pump" which removes electrons from the positive electrode and supplies electrons to the negative electrode. Those ions in solution which can be forced to take electrons by the electric pressure (voltage) which is applied will do so and become the free element. The salt solution contains both sodium ions and hydrogen ions. But, since sodium can force hydrogen ions to accept electrons, it follows that only hydrogen ions will take up electrons under these conditions. Thus during the electrolysis only hydrogen will be released at the negative electrode (cathode). For every hydrogen ion which is so changed there will remain in solution an hydroxyl (OH-) ion since these are formed from water in equal numbers.

Let us consider the positive electrode and the changes which occur there during electrolysis. The negatively charged ions which are present in the solution are given a chance to give up



Courtesy of the Monsanto Chemical Company

Fig. 43. Battery of Electrolytic Chlorine Cells

their extra electrons and become the free atoms of the element. If any current at all flows through the solution some of the negative ions are forced to give up their extra electrons. Those ions which give up these electrons most easily are the ones which will be changed to the free element. The negative ions present in a salt solution are chloride ions (Cl⁻) and hydroxyl ions (OH⁻). Of these, the chloride ions will give up electrons more easily. Thus chlorine is released at the positive electrode (anode) and appears as a gas.

Formation of Sodium Hydroxide. It has been indicated above that the sodium ions and the hydroxyl ions remain in solution during the electrolysis of sodium chloride in water. This solution which remains is highly caustic and, if the water is evaporated, the solid sodium hydroxide (NaOH) is obtained.

Reaction of Chlorine with Sodium Hydroxide. The

chlorine which is formed at the positive electrode (anode) is slightly soluble in water. As a result, some of it comes into contact with the sodium hydroxide which is present. These substances react to form sodium hypochlorite (NaOCl) which is very useful as a germicide and bleaching agent.

However, if chlorine and sodium hydroxide are desired it is necessary that these two substances be kept apart. Special

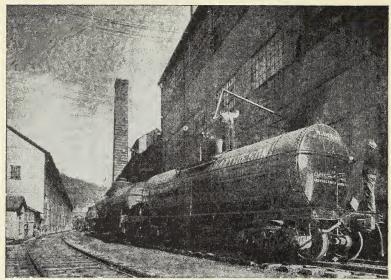
equipment has been designed to accomplish this.

Thus, from the electrolysis of a cold solution of salt we may obtain four distinct substances. At the positive electrode (anode) chlorine gas is evolved; at the negative electrode (cathode) hydrogen gas is evolved; in the water solution sodium hydroxide is formed; if the chlorine is permitted to mix with the solution sodium hypochlorite is formed.

Sodium Hydroxide. The importance of sodium hydroxide is indicated by the fact that more than 800,000 tons of it are consumed within the United States each year. These uses are quite widely distributed as will be seen from the partial list.

Soap	104,000 tons	Lye	46,000 tons
Rayon and pho-		•	
tographic film	174,000 "	Paper and pulp	46,000 "
Chemicals	130,000 "	Textiles (and mer-	
		cerized cotton)	43,000 "
Petroleum		Rubber reclama-	
refining	95,000 "	tion	13,000 "

While sodium hydroxide is relatively expensive when compared with other alkaline substances (lime, sodium carbonate) which are used by industry, it finds the use it does because it is such a strong base. That is, it is very soluble in water and it gives a high concentration of hydroxyl ions (OH⁻) in the solution. Soap is produced by heating animal or vegetable fats with such a solution. Sulfur compounds which naturally occur in petroleum are carried over into the gasoline. Their odor, as they come from the automobile exhaust, would make Sunday



Courtesy of The Mathieson Alkali Works Inc.

Fig. 44. Loading Tank Cars with Sodium Hydroxide Solution

driving intolerable. The use of sodium hydroxide during the refining process aids in the removal of these compounds. In the manufacture of much of the gasoline today there is produced a considerable amount of gum-forming materal which tends to clog the carburator if it is not removed. The removal of this is accomplished through the use of sulfuric acid. The acid is then removed with sodium hydroxide. Most of the rayon manufactured is produced by the *viscose process* in which cellulose (cotton fiber or wood fiber) is treated with sodium hydroxide and carbon disulfide. Cotton thread which has been treated with sodium hydroxide solution and then stretched to dry is said to be *mercerized*. It is stronger and has greater luster than the original fibers.

Sodium Carbonate. Long before the discovery of electrolytic sodium hydroxide, another alkaline material, sodium carbonate (Na₂CO₃), was produced from salt. Prior to the latter part of the eighteenth century the only source of alkali was a natural deposit of sodium carbonate which occurred along the shores of certain lakes in Egypt. This material was much

needed in the manufacture of glass and soap. During the wars of the time the French had trouble getting the amounts of this substance they desired and they offered a prize to anyone who would devise a method for its production from salt. They were sure that this was possible since salt and sodium carbonate each contained the element sodium. A chemist by the name of Leblanc solved the problem. Instead of receiving the prize, Leblanc saw his small factory confiscated by the Committee of Public Safety. The process was later carried to England where it was improved and used for more than fifty years.

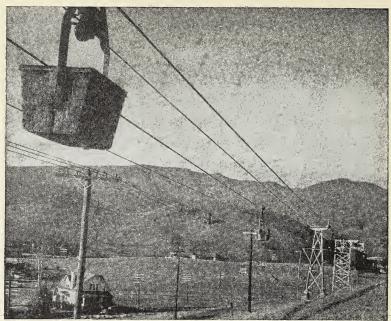
The Solvay Process. Another process for the manufacture of sodium carbonate from salt was proposed by Fresnel as early as 1811. He suggested the reaction between sodium chloride and ammonium bicarbonate.

The sodium bicarbonate (NaHCO₃) is not very soluble in water and would be expected to precipitate out as a solid. Sodium carbonate may be prepared from it. Compounds of ammonia were extremely scarce in those days and the proposed method was not accepted.

In 1863, a Belgian chemist, Ernest Solvay, developed this process and made it work satisfactorily. The sodium carbonate so produced was purer than that made by the Leblanc method and it was much cheaper. He started with a saturated solution of salt in water. Into this was passed ammonia gas as long as it would be dissolved. The ammonia was obtained by the distillation of coal though at the present time it is made largely by a synthetic process. Into the solution which was saturated with salt and ammonia he then passed carbon dioxide. This he obtained from the heating of limestone (CaCO₃).

The solution was kept cold as the carbon dioxide bubbled in and the sodium bicarbonate precipitated. We may represent the total reaction with an equation.

NaCl+NH₃+CO₂+H₂O→NaHCO₃ (sodium bicarbonate) + NH₄Cl



Courtesy of The Mathieson Alkali Works Inc.

Fig. 45. Aerial Tramway for the Delivery of Limestone

The limestone is carried almost eight miles for use in the manufacture of soda ash.

The precipitated sodium bicarbonate is easily converted to sodium carbonate by heating.

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

The sodium carbonate so prepared is exceptionally pure.

This Solvay process has been quite successful. If we examine the various steps carefully some of the reasons for its success will become apparent. The carbon dioxide used in the process comes from cheap limestone from which it is produced by heating in a furnace known as a kiln. There is some sale for the extra lime as a building material and as a cheap source of alkali. The ammonia necessary is usually obtained as a byproduct in the manufacture of fuel gas and coke from coal. After the formation of the sodium bicarbonate this ammonia appears in solution as ammonium chloride and as such is of no



Courtesy of The Mathieson Alkali Works Inc.

Fig. 46. Calcium Carbonate in the Form of Oyster Shells
Millions of tons of these shells are available for use in the manufacture
of lime.

further use to the process. However, by treating this solution with the lime, formed during the preparation of the carbon dioxide, the ammonia is released and may be fully recovered for use.

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$$
 (calcium chloride)

Since the ammonia is the most expensive substance used in this process it is quite important that it be recovered. Since the so-dium bicarbonate produced is quite pure there is little expense of purification involved. The carbon dioxide which is released when the bicarbonate is heated finds its way back into the process and is used over again. The only thing involved in the entire process which does not find ready use or sale is the calcium chloride. This substance absorbs moisture from the air and becomes liquid as a solution. Because of this it finds a small sale to keep down dust on roads and in mines.

Baking Powder. Some of the sodium bicarbonate is sold to

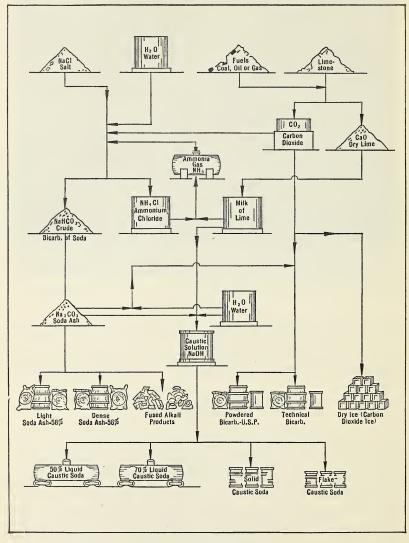


Fig. 47. Flow Chart of Solvay Soda Process

producers of baking soda who sell it for household use. This sells at retail for only a few cents per pound. Hence the processes involved in its manufacture must be easily carried out and quite inexpensive. The principal use of the baking soda is that of an aerating agent in baking (putting the bubbles in bread and rolls). If an acid comes into contact with sodium bicarbonate it reacts to form carbon dioxide. The liberation of carbon dioxide within the dough causes small bubbles to form and when these are heated, they expand to give the porous structure to the baked breadstuff. Baking powder contains sodium bicarbonate mixed with some solid which acts as an acid when dissolved in water. This acid may be cream of tartar, which is potassium acid tartrate, or it may be an acid phosphate such as NaH2PO4. Some types of baking powder contain sodium aluminum sulfate which reacts with water to form a very little sulfuric acid.

$$2NaAl(SO4)2 + 6H2O \rightarrow Na2SO4 + 2Al(OH)3 + 3H2SO4$$

The small amount of acid formed reacts with the bicarbonate to form carbon dioxide.

$$H_2SO_4 + NaHCO_3 \rightarrow NaHSO_4 + H_2O + CO_2$$

Baking powder must be kept very dry, and so some substance such as starch or flour is usually mixed with it to help accomplish this.

Electrolytic Process. The newest method for the preparation of sodium carbonate is the electrolytic process. The sodium hydroxide produced by the electrolysis of a salt solution is treated with carbon dioxide. This converts the hydroxide to the carbonate.

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$$

In this process they do not bother to get out the sodium hydroxide but simply add carbon dioxide to the solution during the electrolysis. The cost of electrical energy in most areas of the United States prevents the greater use of this method.

Uses of Sodium Carbonate. The annual production of so-

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dium carbonate in the United States runs well over two million tons. Its uses are distributed over a variety of industries. Some of the most important are listed.

Glass manufacture	670,000 tons
Chemicals	325,000 tons
Soap	210,000 tons
Paper	100,000 tons
Water softeners	65,000 tons
Textiles	50,000 tons
Petroleum refining	25,000 tons

In water solution, sodium carbonate gives a basic reaction and finds a large use in the manufacture of soap in place of sodium hydroxide. Many of its uses depend upon its reaction with water which is called *hydrolysis*.

The NaOH formed is highly ionized and thus the solution is strongly basic. This property is utilized in detergents (cleaning agents) such as soap powders which contain some soap mixed with sodium carbonate. Also it is this alkalinity of its solution which brings about the use of sodium carbonate in the manufacture of paper, textiles, and the purification of petroleum.

The low cost of sodium carbonate makes it a starting point for many other chemical substances. It is easily converted to other compounds, which adds to its usefulness. A process for the manufacture of sodium hydroxide uses sodium carbonate with a mixture of lime in water. The lime reacts with the water to form calcium hydroxide which in turn reacts with the sodium carbonate to form sodium hydroxide and calcium carbonate.

$$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaOH$$

The calcium carbonate is insoluble in the mixture and simple filtration removes it from the sodium hydroxide. This method provides more than half of the total sodium hydroxide produced.

It will be recalled that sodium carbonate is used in the softening of water (Chapter 12). The carbonate ions (CO_3^{--}) unite with the calcium and magnesium ions present in the water to form the carbonates of these which are insoluble.

If sodium carbonate is treated with sulfur dioxide in water it forms sodium sulfite (Na₂SO₃), used to remove chlorine from cloth which has been bleached with this gas. Sodium sulfite is also used to dissolve the lignin, or gluelike material, from wood fibers in pulp manufacture, and as an aid in the tanning of leather. If the sulfite is boiled with sulfur it is converted to sodium thiosulfate (Na₂S₂O₃) which is the common "hypo" of the photographer. The exposed photographic film is placed in the



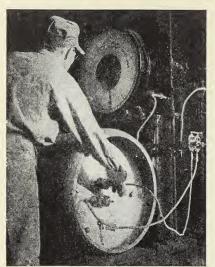
Courtesy of The Mathieson Alkali Works Inc.

Fig. 48. Loading Sodium Carbonate in Bulk

"hypo" solution after it has been developed to bring out the image. The "hypo" dissolves any silver salts which remain in the film and thus the image becomes permanent.

Chlorine. Chlorine which is liberated at the anode during the electrolysis of salt solutions has become important during recent years. Its greatest use is for the bleaching of cotton, linen, and wood pulp from which paper is made. Wool and silk are destroyed by chlorine and thus it cannot be used to bleach these fibers. Cotton and linen are slightly affected by the bleaching process. Hence it is quite necessary that all of the chlorine be removed from the fibers. To do this the material is washed with water which contains either sodium sulfite or sodium thiosulfate. These substances act as *antichlors* and convert all of the excess chlorine into sodium chloride.

The Bleaching Process. It is curious that dry chlorine will not bring about the bleaching of fibers, but if the fibers are wet, the bleaching process proceeds normally. It has been found that chlorine reacts with water to produce hydrochloric



Courtesy of the Monsanto Chemical Company

Fig. 49. Filling a Cylinder with a Ton of Liquid Chlorine

acid and hypochlorous acid (HOCl).

Cl₂ + H₂O → HCl + HOCl In the presence of easily oxidized substances the hypochlorous acid decomposes as fast as it forms and in so doing releases oxygen one atom at a time. This atomic oxygen is very reactive and attacks the coloring matter to give colorless substances.

$HOCl \rightarrow HCl + O$

It has been shown that most colored dyes and other coloring matter which occur in the fiber are ren-

dered colorless by their union with oxygen so furnished.

Sodium Hypochlorite. The application of chlorine as a household bleaching agent has been promoted by the appearance of a number of bleaching solutions in the retail stores (Chlorox, Hilex). Most of these solutions are formed by passing an electric current through a sodium chloride solution which is kept stirred in order that the chlorine and the sodium hydroxide may mix. This produces sodium hypochlorite (NaOCl) which is an effective bleaching agent and which may be used with safety in the home. Most of these products are plainly marked in order to warn against their use in contact with wool or silk. Sodium hypochlorite owes its bleaching action to the oxygen which is released as with chlorine solution.

In actual practice it is the hypochlorite rather than the free chlorine which is used for large-scale bleaching since the alkaline nature of the hypochlorite solutions promotes the bleaching action. In many instances lime is used together with chlo-

rine to form calcium hypochlorite which also is an effective bleaching agent.

Antiseptic Value. The same properties of chlorine and hypochlorites which make these substances good bleaching agents also endow them with unusual antiseptic properties. The very reactive oxygen which is released by these substances attacks disease germs as well as other organic material. During the first World War a solution known as Carrel-Dakin solution containing sodium hypochlo-



Courtesy of the Monsanto Chemical Company

Fig. 50. Loading Cylinders of Liquid Chlorine on a Flat Car

rite together with sodium chloride was used extensively in the treatment of wounds with remarkable success. It seems well established that such solutions, when properly applied, are capable of considerably shortening the healing time of wounds.

It was also noted during that World War that workers in chlorine plants did not suffer from influenza as did others. Experiments which were carried out indicated that very mild doses of this gas may serve with some people as an effective preventative of this disease and some other respiratory diseases though it is of doubtful value as a treatment after the disease begins to take effect.

Water Purification. The purification of water consumes a considerable amount of chlorine. For this purpose the liquid chlorine is supplied in steel tanks of convenient size to facilitate handling. The decrease in the outbreaks of such diseases as typhoid fever and dysentery are almost entirely due to the use of chlorine in water supplies and in swimming pools. The actual amount of chlorine required is very small, since, in most cases, it requires only one half to one and one half parts



Courtesy of The Mathieson Alkali Works Inc.

Fig. 51. Loading a Tank Car with Liquid Chlorine

of chlorine in one million parts, by weight, of water to destroy all of the dangerous bacteria which may be present. The chlorine so applied is converted harmless compounds, and, unless some industrial wastes are present or the chlorine is used in excess, there is no resultant taste or odor. For many years calcium hypochlorite was used for water treatment but the application chlorine is so easily carried out that the hypochlorite method is disappearing.

Other Uses. Chlorine is

a useful industrial chemical. The liquid known as "carbona," with which dry cleaning may be carried out with no fire or explosion danger is carbon tetrachloride (CCl₄). Similar compounds are used in the extraction of lubricating oils in an attempt to produce better lubricants. Various dyes, explosives, and disinfectants also are prepared with the aid of chlorine.

Much has been written concerning poison gas which was used in the first World War and which probably will be used in the war now going on. Most of these gases contain chlorine. The first gas used was chlorine itself. In ordinary amounts it serves as a choking poison. Among other substances used have been phosgene (carbonylchloride COCl₂), mustard gas (dichlordiethyl sulfide (C₂H₄Cl)₂S), and various tear gases con-

taining chlorine. These tear gases find much use for stopping riots and for deterring safe robbers.

Hydrogen Chloride. If the hydrogen and the chlorine which are produced from the electrolysis of solutions of sodium chloride are allowed to react together hydrogen chloride is produced. This substance is a gas but is very soluble in water. The water solution is called hydrochloric acid. The same substance is produced if salt is treated with sulfuric acid.

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$$

Hydrochloric acid has been an important industrial and medical chemical for a long time and its importance is constantly increasing.

When iron is to be coated with zinc, as in *galvanized iron*, or with tin, as in *tin plate*, or with various enamels it must be quite clean and free from all oxides (rust) of iron. This is accomplished by dipping the iron in hydrochloric acid just before the coating process is carried out.

In the manufacture of corn syrup, from cornstarch, hydrochloric acid is used to aid in the conversion of the starch to glucose. This acid is also used in the preparation of glue from animal tissues and for the purification of animal charcoal for use in the clarification of sugar syrup. Hydrochloric acid enters into the manufacture of at least one artificial rubber (Neoprene).

Hydrochloric acid is used to increase the flow of oil in oil wells. Many times the oil-bearing layer contains limestone and this material is dissolved by the acid. This leaves a porous structure of undissolved stone which serves to increase the surface from which oil may come. Many old wells have been brought back into production by this treatment.

SUMMARY

All water solutions of salts contain hydrogen ions derived from the water. During the electrolysis of these solutions it is the relative affinity for electrons which determines whether it is the metal of the salt or hydrogen which is released at the negative electrode. The same considerations determine whether it is the negative ion of the salt or the hydroxyl ion from water which gives up electrons at the positive electrode. The electrolysis of sodium chloride in water liberates hydrogen and chlorine leaving sodium ions and hydroxide ions in solution. This solution gives sodium hydroxide when evaporated.

Sodium hydroxide is an important chemical in the production of soap, rayon, photographic film, petroleum products, paper, and other compounds of sodium.

Chlorine is useful as a bleaching agent, in water purification,

and in the manufacture of other compounds.

Sodium hydroxide and chlorine react together to form sodium hypochlorite which is useful in bleaching and as an

antiseptic.

With carbon dioxide, sodium hydroxide reacts to form sodium carbonate. This is useful in the manufacture of glass, soap, paper, other compounds of sodium, textiles, petroleum products, and in water softening. Sodium carbonate may also be made from salt by the Solvay process. This method takes advantage of the reaction between salt, water, ammonia, and carbon dioxide to form sodium bicarbonate. This sodium bicarbonate is used as baking soda or is heated to give sodium carbonate. The Solvay process is possible economically because it uses cheap raw materials and recovers all of the by-products which may be used over again.

Baking soda is used in baking because it liberates carbon

dioxide with acids. This aerates the baked food.

Sodium carbonate may be used for the preparation of most other compounds of sodium. It is used with lime in the manufacture of sodium hydroxide; with chlorine in the manufacture of sodium hypochlorite; with sulfur dioxide in the manufacture of sodium sulfite for the removal of chlorine from textiles after bleaching; and with sulfur dioxide and sulfur in the manufacture of sodium thiosulfate (hypo) for photographic use.

The bleaching of cloth by chlorine or by hypochlorites

takes place because of the active oxygen which these substances release when treated with water.

The use of chlorine in water purification is notable because so little of it is required to destroy practically all of the bacteria present.

Hydrogen and chlorine will react to form hydrogen chloride which dissolves in water to form hydrochloric acid. This acid which has considerable industrial use may also be made by treating salt with sulfuric acid. A considerable amount of hydrochloric acid is used in the treatment of oil wells to increase their production.

REVIEW QUESTIONS

- 1. If metallic sodium were released at the negative electrode during the electrolysis of salt in water, what should happen to it at once?
- 2. What is the source of hydroxyl ions for the production of sodium hydroxide by the electrolysis of sodium chloride solutions?
- 3. To what is the negative charge of the chloride ion due, according to our modern idea of the atom? Why is the sodium ion positive?
- 4. What four substances may be direct products from the electrolysis of sodium chloride solutions? List the uses of each of these products.
- 5. For what reason do we say that sodium hydroxide is a strong base?
- 6. Account for the fact that sodium carbonate in solution behaves as a base.
- 7. In what common household products would you expect to find sodium hydroxide? Sodium carbonate? Sodium hypochlorite?
- 8. Outline the Solvay soda process. Why is it possible to get the sodium bicarbonate out from the other substances present?
- 9. List the source of each substance used in the Solvay process.
- 10. Show clearly the enonomic advantages of the Solvay process.
- 11. Give the method for converting sodium bicarbonate to the carbonate.

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- 12. What sort of substances must be present in baking powder? What is the purpose of baking powder?
 - 13. What are the chief uses of sodium carbonate?
- 14. How may sodium hydroxide be made from sodium carbonate?
 - 15. Why is sodium carbonate used in water softening?
- 16. How do we explain the bleaching action of chlorine and hypochlorites?
- 17. Why is it necessary to remove the excess of chlorine in cloth after the bleaching process is complete? How is this done?
 - 18. What is Carrel-Dakin solution? For what is it used?
- 19. For what purpose is chlorine used in water purification? What have been the results of its use?
 - 20. Give some uses for hydrogen chloride. How is it made?

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- See also any text on General or Introductory Chemistry.

SAND, CERAMICS, CEMENT

The most abundant element in the crust of the earth is oxygen, which makes up one half of the total weight. Next to oxygen is the element silicon which accounts for the next one fourth of the total weight. The compounds of silicon which occur in nature form about 87 percent of the solid crust of the earth and are widely distributed among the rocks and soil of all kinds. Silicon is the central element of the mineral kingdom, just as carbon plays the fundamental part in the animal and

plant kingdoms.

One of the most abundant compounds of silicon is its oxide which many of us know best in the form of small particles called sand. If these sand particles have been cemented together by pressure under earth in a layer of rock they are called ordinary sandstone. Frequently the dioxide of silicon occurs in large crystals which are known as quartz. Among the crystalline forms of silicon dioxide there are the semi-precious stones amethyst, onyx, agate, flint, and opal, the properties and colors of which are due to slight impurities. Other compounds of silicon occur in the form of clay, granite, shale, mica, asbestos, topaz, and feldspars.

Quartz. Chemically, quartz is pure silicon dioxide. It is noted for its crystal clearness and for the curious fact that it transmits light even better than does the air. If quartz is heated to a rather high temperature it softens and the molten mass may be shaped into various forms such as laboratory apparatus, tubes, and sheets. Because in the melting dissolved gases fill the material it becomes opaque to light unless it is melted under greatly reduced pressure to allow the gases to escape. After such treatment the material resembles ordinary glass except that

it is not broken by sudden temperature changes; it is unusually resistant to chemical action; and it transmits ultraviolet light. This last property has brought about its use in place of window glass in certain instances where the beneficial rays of the sun are desired indoors, and in the manufacture of ultraviolet lamps and certain microscopic and telescopic lenses.

Chemical Behavior. Silicon dioxide (silica) is an acidic oxide and as such it reacts with alkali to produce a salt. When heated with sodium hydroxide or with sodium carbonate

sodium silicate (Na₂SiO₃) is formed.

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$$

The volatile carbon dioxide escapes from the molten mixture. The resulting sodium silicate is soluble in water and when the water solution is allowed to evaporate it leaves the sodium silicate as a glassy material. Because of this and its solubility in water it is called water glass. It is used by some manufacturers of corrugated paper boxes as a glue to hold the layers of paper together and is then known as silicate glue. It has long been used in the preservation of eggs. The eggs are covered with a solution of water glass and the sodium silicate closes the pores in the shells so that air cannot enter and cause the egg to spoil.

If limestone is heated with silicon dioxide, calcium silicate is formed by a reaction entirely similar to that which produces

sodium silicate.

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$$

Here again the volatile carbon dioxide is driven off. The calcium silicate formed is a glasslike material and like sodium silicate it has no definite melting point but slowly softens as it is heated.

Glass. If limestone and sand mixed with sodium carbonate are heated in a suitable furnace the entire mass slowly melts to form glass. Each substance present lowers the melting point of every other substance present. As a result the glass produced begins to melt considerably below red-heat. Such soda-lime



Courtesy of the Libbey-Owens-Ford Glass Company

Fig. 52. 3,000 Pounds of Molten Glass

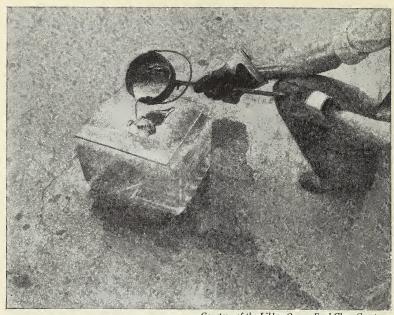
Heated to a temperature of 2800 degrees Fahrenheit, silica, soda ash and other components of the "batch" fuse and acquire transparency. This photograph shows a clay pot containing 3,000 pounds of molten glass being removed from the melting furnace to be rushed to the casting table.

glass is used for ordinary bottles and for windows. It consists of sodium silicate, calcium silicate, and unchanged silicon dioxide. If one could write a chemical formula for the mixture it would be somewhat near Na₂SiO₃·3CaSiO₃·2SiO₂, though this composition may be varied. For ordinary glass some of the sodium carbonate is replaced by sodium sulfate which can also react with silicon dioxide with the evolution of volatile SO₃ (sulfur trioxide).

$$SiO_2 + Na_2SO_4 \rightarrow Na_2SiO_3 + SO_3$$

The glass industry consumes more than 400,000 tons of sodium sulfate each year.

If all of the materials are pure the resulting glass is entirely colorless, but as a rule such materials are not to be found.



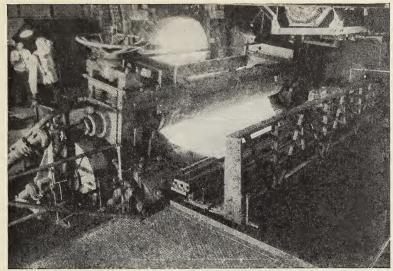
Courtesy of the Libbey-Owens-Ford Glass Company

Fig. 53. Heat-Toughened Plate Glass

A new type of heat-tempered plate glass called tuf-flex is so resistant to thermal shock that molten lead can be poured without damage upon a pane which is resting on a cake of ice. Ordinary glass would be shattered instantly.

Natural sand usually has more or less iron oxide (rust) mixed with it even though it may be in very small amounts, and during the melting process this oxide is converted to ferrous silicate which is green. It is this green coloring matter which contributes the color to old bottles and to window glass. The addition of small amounts of manganese dioxide during the melting of the glass will remove the green color. Some other substances also contribute characteristic colors such as the red of gold glass and of selenium glass and the deep blue of cobalt glass.

Other Kinds of Glass. If we are willing to use our imaginations just a little it may seem possible to write the formula for glass in a slightly different way. Thus the formula Na₂ SiO₃·3CaSiO₃·2SiO₂ may be written as Na₂O·3CaO·6SiO₂ without indicating any change in composition. Actually such



Courtesy of the Libbey-Owens-Ford Glass Company

Fig. 54. Molten Glass Rolls Out

This is the type of machine used in producing extra-heavy plate glass and colored structural glass in the Libbey-Owens-Ford Glass Company plant at Rossford, Ohio. After passing between smoothing rollers at gradually reduced temperature, the glass is annealed in a long lehr and then cut to handling size.

a substance as sodium oxide (Na₂O) does not exist free within the glass, but it is sometimes quite convenient to consider the three oxides as being separate as shown. Now all glass contains SiO₂ as the chief ingredient, but the actual amount of this substance may be varied to a great extent. In place of the sodium oxide one may substitute potassium oxide which results in a hard glass of unusual clearness. It may be used for optical purposes. By putting in lead oxide in place of the calcium oxide and potassium oxide in place of the sodium oxide, there is obtained a heavy, sparkling glass from which cut ware is made. This same glass serves for the production of artificial (paste) gems.

Because of conditions in certain situations where it is desirable to use glass it became necessary to develop a glass with a low coefficient of expansion. By this we mean that the glass

changes very little in size as the temperature is changed. Glass is a very poor conductor of heat and if one side of a glass vessel is strongly heated the expansion of the hot side may pull the molecules of the cold side apart before they have time to warm up. That is what happens when we fill a cold milk bottle



Courtesy of the Libbey-Owens-Ford Glass Company

Fig. 55. Under the Rotors

Bathed in a mixture of sand and water, the blanks of glass pass under huge rotors in the Libbey-Owens-Ford Glass Company plant at Rossford, Ohio. This removes roughness and makes the two surfaces precisely paralel. Then comes the polishing with iron oxide "rouge" under rotors lined with felt. The grinding and polishing gives plate glass its lustrous quality and freedom from the waviness of ordinary window glass.

with hot water and it shatters in the sink. In a similar manner, if a piece of hot glass is cooled quickly, the cooling may cause the molecules to be pulled apart before the whole thickness of glass contracts. Now if the glass changes very little with temperature these dangers are considerably lessened and this is the basis for the use of low-expansion glass. The brand of glass known as "Pyrex" is such a glass and reprereal scientific a achievement. We can use it in the scientific laboratory or in the kitchen and subject it to sudden changes of heat and cold without shattering. More-

over it is almost unaffected by many chemicals which attack ordinary glass. In this glass the metallic oxides are almost entirely omitted and the SiO₂ is increased to 81 percent. In place of most of the calcium, sodium, or potassium oxides about 12 percent of boron oxide (B₂O₃) is used. In addition the glass contains a little aluminum oxide (Al₂O₃).

Glass Working. In the manufacture of glass articles the molten glass is either pressed or blown into shape by hand or with compressed air. When done by hand the workman gathers a ball of molten glass on the end of a hollow pipe and using his cheeks as a bellows he fashions the article with air pressure from his lungs while he turns the pipe. Naturally, such operations require a great amount of skill. Many articles such as bottles may be so blown, but to make for speed and

uniformity a mold is used to constrict the glass to a definite size and shape. All glass must be cooled very slowly for a long period of time to prevent internal strains which cause breakage. Such careful cooling is called annealing.

Within recent years the use of machines has largely replaced manpower in blowing glass. A few years ago much of the window glass was blown by hand into long tubes some five or six feet in length and about a foot in diameter. These tubes were cut off at the ends, split down the side, and flattened by heating and smoothing. The machine blown window glass is made in cylinders as much as forty feet long



Courtesy of the Libbey-Owens-Ford Glass Company

Fig. 56. For Better Vision and Safety

Tests conducted by Dr. A. H. Ryan, Chicago physiologist, showed that looking through ordinary window glass, such as that at right in this photograph, produces 62 per cent greater eye strain than looking through precision safety plate glass, through which the chart at left may be seen. Many models of 1941 cars are being equipped with the high-test safety plate glass.

and three feet in diameter. These, too, are split down the side and flattened. Methods are now in use whereby a sheet of window glass is drawn directly from the molten glass as a wide ribbon and this has almost entirely replaced the blown product. Plate glass is made by pouring the molten glass on a table where it is rolled to uniform thickness and then polished.

Optical Glass. Glass from which various optical instru-

ments are to be made must be quite uniform and highly transparent. Only the best of materials are used and small pots serve as the containers for the individual batches. During the melting process, the mixture is stirred to obtain uniformity and then the pot is annealed for a long period of time. The entire mass is broken up and individual pieces are carefully ground to the desired shape. For some of the cheaper instruments the glass is softened and molded by means of pressure molds.

CERAMICS

Bricks and Pottery. Just as the more or less pure components of glass may be mixed and melted together to form artificial silicates, the naturally occurring impure silicates such as clay may also be melted. The nature of the finished product will depend upon the material used and upon the temperature of the furnace in which the substance is heated. With some forms of good clay known as kaolin, which may be considered as Al₂O₃·2H₂O·2SiO₂, the finished product is white and glasslike in the form of fine porcelain. The less pure forms of clay produce varying types of products from bricks to pottery. In the industries which produce these things the article is shaped from the moist clay, and then, after drying in the air, it is fired to the proper temperature to give the strength and durability required.

There is much more to the manufacture of clay products than merely shaping the article and then heating it. The clay particles must be in the colloidal state of division. This is accomplished by aging the clay in the presence of moisture together with some deflocculating agent. For bricks this deflocculating agent may be obtained from wet straw which probably furnishes tannin. The ancient Egyptians realized the importance of this process. Frequently several different types of clay may be mixed before the desired properties are obtained. For earthenware the firing temperature is about 1270° C. but for the more glasslike articles of porcelain the

temperature may reach 1400° C. or even higher. This temperature is the same as 2550° F. and is (as we can imagine) quite hot.

The heating process drives off the water which may be present with the clay. It also drives off the water which is combined as a part of the clay molecule. This leaves a skeleton form which is porous. If the heating continues until melting actually occurs it becomes no longer porous, but the product shrinks. If the finished product is to be glazed, as in pottery and table china, this is done in one of several ways. Cheap articles are glazed by throwing salt into the furnace. The high temperature vaporizes the salt and it combines with the silicates in the surface of the material. This lowers the melting point and the outside of the article melts. When cool, the glaze surrounds the porous material like a casing of glass. For better articles the fired material is dipped or sprayed with some other silicate or mixture which will give a glass when again heated. Care must be taken to be sure that the finished glaze will not crack away from the body of the ware under normal changes in temperature. Colored glazes are produced by adding metallic oxides to the glazing mixture.

MORTAR

While discussing the common building material, bricks, it seems proper to include something about the binding agent which is used to hold the bricks of a building together. The most commonly used binding agent is mortar which is made by mixing sand with lime and water. Quicklime is produced by heating limestone (calcium carbonate, CaCO₃) in a kiln which decomposes it to form lime (calcium oxide, CaO) and carbon dioxide:

$$CaCO_3 \rightarrow CaO + CO_2$$

Quicklime combines with water to produce slaked lime (hydrated lime, or calcium hydroxide):

$$CaO + H_2O \rightarrow Ca(OH)_2$$

If properly mixed with water this calcium hydroxide becomes colloidal and forms a stiff mass which may be mixed with sand and spread between the bricks. Slowly the mortar loses water and begins to absorb carbon dioxide from the air. These two processes result in the formation of a layer of sand particles surrounded by interlocking crystals of calcium carbonate due to the reaction of the lime with the carbon dioxide:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Most of the excess water is lost within a few days but the reaction with carbon dioxide may proceed for many months.

Plaster is a modification of mortar. The changes which take place during its drying are essentially the same as with mortar. In order to speed up the hardening of plaster it is a common practice to place charcoal burners in a newly plastered house. These furnish a large amount of carbon dioxide and thus hasten the formation of calcium carbonate.

CEMENT

Cement differs considerably from mortar. This material was first discovered by the early Romans who found a natural rock which would harden with water after being burned and powdered. This supply of natural cement rock, called *possuolana*, was soon exhausted and another source had to be found. In 1824 an Englishman discovered a mixture of materials that would give similar results, and since the finished stone looked like a certain kind of natural rock found at Portland, England, he named it Portland Cement. One patent was issued for the manufacture of this substance which called for its production from the road dust of certain stone-covered roads.

The essential ingredients of this Portland cement are limestone and clay. Certain other limestone materials can be used and shale may be substituted for the clay. These materials in exactly correct proportions are ground together and heated. The grinding is usually done wet and the wet mixture fed into a furnace where it is first dried and then heated until it just begins to melt. The furnace used is a rotating one much like an exceedingly long barrel 10 feet in diameter and 250 feet long. As it rotates, the partly melted particles are rolled into small balls and are called clinker. This clinker is ground to an extreme degree of fineness, mixed with a small amount of gypsum (CaSO₄·2H₂O) which acts to retard the time of setting, and sold as cement.

With water, the cement seems to undergo many complicated changes. However, it is fairly certain that the water enters into chemical reaction with the substances present in the cement, and the product formed is hard and adhesive. In this respect cement differs from mortar because it must have water in order to harden. If the weather is too hot, or dry, additional water must be added each day to insure the proper hardening. In the building of roads great precautions are taken to insure an adequate water supply for the hardening cement. There are two distinct steps in this process. First the cement "sets" to a jellylike mass which must not be disturbed, but at the time of the "set" there is no strength in the material. This is somewhat like the colloidal condition of the clay for pottery and the lime for mortar. Then the water slowly reacts with the mixture and the strength of the cement begins to appear. The maximum strength does not develop until many days or weeks after pouring. There are rapid-setting cements on the market which are chemically speeded up to attain their maximum strength in a couple of days. These are a great boon to building and paving where time is an important factor. These have been used too short a time as yet to say whether they are as good as the regular cement. However, nothing indicates otherwise.

From the description of the manufacturing process one can get some idea of what is present in the cement. If we remember the discussion on glass we would expect to find calcium and aluminum silicates in the cement. While the composition can be varied somewhat, yet there are certain restrictions which must be rigidly observed. The percentages of iron oxide and aluminum oxide must be controlled as well as the relation between the calcium oxide and the silicon dioxide.

SILICON CARBIDE

It would be improper to close this chapter without mentioning silicon carbide which is commonly known as carborundum. It was back in 1885 that Acheson mixed clay and charcoal and heated the mixture with an electric arc created within the mass. He obtained beautiful crystals of various colors which were quite iridescent. These he sold at first as gems at a high price. But, because of their hardness, he was able to sell them by the ton at a few cents per pound and make more money. The hard crystals were composed of silicon and carbon and their composition was best expressed by the formula SiC. This substance is now known as carborundum and has for many years been one of our most useful grinding agents. The mass production of modern machinery such as automobiles would be impossible without this or a similar material because most moving parts must be ground to fit. For use, the crystals are cemented together in the form of a wheel or they are blown as finer or coarser dust onto a cement-covered paper or cloth.

At the present time carborundum is made several tons at a time in large brick boxes about seven feet wide, seven feet high, and as much as fifteen feet long. A mixture of sand and carbon (coke) together with salt and sawdust is placed in the box and the electric current is run through the mixture between carbon electrodes placed in the ends of the box. The reaction takes place at the high temperature produced by the resistance of the mass to the flow of the heavy current.

$$SiO_2 + 3C \rightarrow SiC + 2CO$$

The salt melts and acts as a liquid "flux" and the sawdust keeps the mass porous.

SUMMARY

The element, silicon, accounts for one fourth of the total weight of the earth's crust. It always occurs in the combined state. Its compounds total 87 percent of the solid crust of the earth.

Pure silicon dioxide is called quartz. Sand consists of small particles of impure quartz. The melting point of quartz is quite high. Pure quartz permits the passage of ultraviolet and visible light.

Quartz is an acidic oxide and thus reacts with alkalies to form salts. Glass is a mixture of silicates with no definite melting point. Window glass contains the silicates of sodium and calcium. Other glass may contain the silicates of lead and potassium. Pyrex glass has a low thermal expansion. It is largely silica mixed with the silicates of boron and aluminum.

Bricks and pottery are made from the naturally occurring silicates found as clay. Heating converts these to insoluble and hard silicates which resemble glass. The type of product depends upon the type of raw material used and the temperature to which it is heated. The glaze is composed of more easily melted silicates with a thermal expansion near that of the body of the ware.

Mortar is a mixture of colloidal calcium hydroxide and sand. It hardens by loss of water together with a union with carbon dioxide from air to form calcium carbonate.

Cement is made by heating together definite proportions of limestone and clay. The resulting material is finely ground. With water this produces new substances which harden and hold together by forming interlocking crystals.

Silicon carbide is produced by heating sand and carbon together in an electric furnace. The product is crystalline and extremely hard. It is used as an abrasive.

REVIEW QUESTIONS

- 1. Carbon and silicon are in the same group in the periodic table. Show some of their similarity by writing the equations for the reactions of their dioxides with sodium hydroxide and with calcium oxide.
 - 2. Why is ordinary glass broken by sudden chilling?
 - 3. What property of Pyrex glass makes it resistant to heat?
- 4. Account for the porous nature of earthenware and the lack of porosity of fine china.

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5. What is the difference between the body of earthenware and the glaze?

6. From what, and how is lime produced? Write the chemical

equation.

- 7. What is the difference between quicklime and slaked lime? Write the equation for the formation of slaked lime from quicklime.
 - 8. What changes bring about the hardening of mortar?
- 9. What is the essential process in the hardening of cement? How does this differ from that of mortar?
- 10. How is silicon carbide made? What is its common name? Of what use is it?

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SULFUR

The use of sulfur extends back beyond 4000 years according to ancient writings. The peculiar blue flame with which it burns, together with the pungent odor which is thus produced, must have made it a picturesque stuff to use in black night mysteries and ceremonies of worship. In addition to its power to kindle human emotions through sight and smell, the ancients realized its practical effect in the bleaching properties of the oxide of sulfur. Later they discovered, too, its use by burning the sulfur as a fumigant. This dates back at least to 1000 B.C. according to the Greek literature. By mixing sulfur with other substances the Chinese discovered gunpowder at least five hundred years before the Christian Era, although they made firecrackers to frighten away demons long before they found out how to propel bullets with it. Early medicine and the treatment of human ills was largely dependent upon sulfur for many centuries. Even present-day medicine has some uses for it. Thus throughout the recorded period of man, sulfur has played a definite part, and, while its uses have changed, its importance has steadily increased.

Occurrence. Sulfur occurs almost everywhere. The materials of which animal cells are composed contain sulfur. This includes human and animal hair, wool, silk, eggs and flesh. In many parts of the earth there are extensive underground streams of water which are saturated with hydrogen sulfide gas, and, when these are penetrated by wells or appear as springs, they yield the so-called sulfur waters. Many invalids go to Hot Springs or Spas "to take the waters" some of which are sulfur, others iron, others still containing chemicals assumed to have therapeutic value. Some of the most important ores

of the metals contain both the metal and sulfur in the form of sulfides. A great amount of iron occurs in the earth as iron sulfide, but this has never yet been worked as a profitable source of iron. When Aetna and other volcanoes blow off their tops and hurl molten lava, ash, and smoke high into the air the volcanic action evolves enormous quantities of sulfur in the form of hydrogen sulfide. This seems to indicate that large deposits of sulfur or its compounds occur deep in the earth.

The element sulfur, in its free form, was discovered on the island of Sicily about four hundred years ago. But it was not until the discovery of sulfuric acid that this deposit became important. Since that time sulfur has been sought from every possible source. The annual production of sulfur and of sulfuric acid has increased enormously. About 1870, while making explorations for oil along the coast of the Gulf of Mexico, the drillers discovered several sulfur deposits at depths of five hundred feet or more. Men went to work at great labor and cost to mine the element. But because, after they got down about a hundred feet, great quantities of poisonous hydrogen sulfide gas came in upon them making them lose consciousness and resulting in death, and because gas masks had not yet been invented to protect them, they had to abandon the work and let the sulfur go untouched. Since the deposits in Sicily occur near the surface, they are readily accessible. It is only necessary to heat the mixture of rock and sulfur above the melting point of the sulfur which then melts and runs away from the contaminating material. For many years this simple method of mining was easily the victor in the race with the American deposits.

The Frasch Process. Herman Frasch came to the United States about 1870 and worked as a pharmacist. He became interested in petroleum refining and had remarkable success at it. Some of the thinking he had done on oil stimulated his imagination about sulfur, and he conceived an idea for getting the American sulfur to the top of the ground. He drilled a

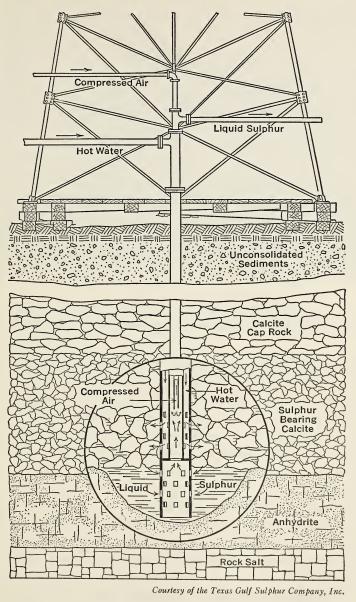
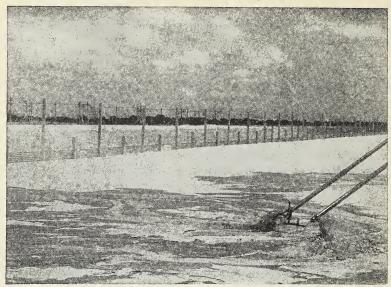


Fig. 57. Sketch Showing Sulfur-Well Piping



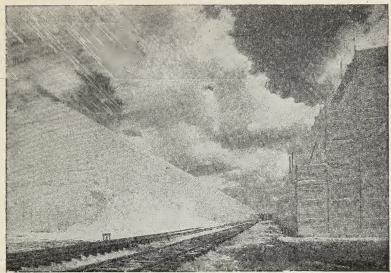
Courtesy of the Texas Gulf Sulphur Company, Inc.

Fig. 58. Sulfur Discharging into a Vat

The delivery pipes swing about to give an even layer of liquid sulfur.

rather large (10-inch) hole into the rock which contained the sulfur and cased the hole with a pipe having perforations near the bottom. Inside this outer pipe were placed two other concentric pipes which went nearly to the bottom. Hot water under pressure and at a temperature above the melting point of the sulfur was forced down the outer space thus provided and it caused the sulfur near the well to melt and to rise in the inner pipes. Compressed air was forced down the center pipe and this caused the sulfur together with water and air to rise to the surface in the third space provided. The molten sulfur was permitted to collect in large crudely constructed boxes or pens where it soon hardened and could be shipped and processed.

This ingenious method of mining has proved a remarkable success and has furnished an ample supply of pure sulfur for the entire world. The open mining deposits in Sicily are still operated by that method as are those in other countries, but



Courtesy of the Texas Gulf Sulphur Company, Inc.

Fig. 59. Sulfur Vats

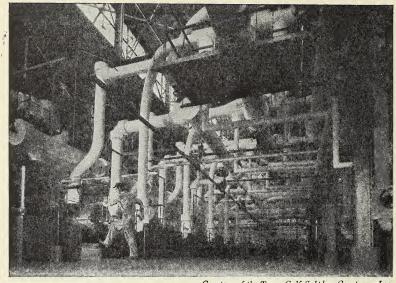
50 Feet High, 175 Feet Wide, 1200 Feet Long. Contain one half million tons of sulfur each. The forms to receive the liquid sulfur are still in place at the top of the vat on the right.

all of these, since the Frasch process, are enabled to continue only through government aid and high tariffs.

Since sulfur is so vital to all industry it is easy to understand why every country desires to have its own sulfur industry in operation all of the time. Its relation to other basic industries also accounts for the changes in volume of sulfur production through the years. In 1930 the United States produced more than two and one half million tons, but in 1932 this dropped to less than one million tons. We frequently see reference to sulfur as a "key" chemical because of its many uses.

Sulfuric Acid. The largest industry which consumes sulfur is the manufacture of sulfuric acid. This substance is probably the most important chemical, with the exception of water, with which industry has to deal and this importance is reflected in the total tonnage consumed.

The following list of the uses of sulfuric acid will give an idea of its importance. The figures are in tons of solution con-



Courtesy of the Texas Gulf Sulphur Company, Inc.

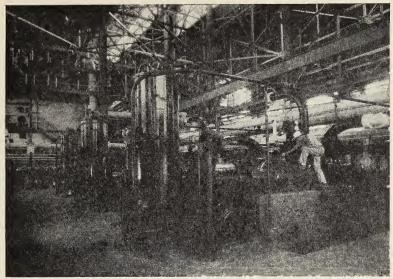
Fig. 60. Pumps and Piping

These deliver the large amount of hot water required to mine sulfur.

taining 63 percent of the acid, H₂SO₄, taken from Chemical and Metallurgical Engineering, February 1940.

0 0	•	
	1938	1939 (estimated)
Fertilizer manufacture	1,920,000	2,100,000
Petroleum refining	1,100,000	1,210,000
Chemical manufacture	800,000	975,000
Coal products (dyes and drugs) .	585,000	740,000
Iron and steel (cleaning)	590,000	980,000
Metallurgy	350,000	570,000
Paints and pigments	430,000	500,000
Explosives	140,000	190,000
Rayon and cellulose film	318,000	400,000
Textiles	90,000	116,000
Storage batteries, etc. (misc.)	355,000	400,000
Total	6,678,000	8,181,000

The weight of this annual production is greater than the combined weight of all the people in the United States. Its value is about \$42,000,000 per year.



Courtesy of the Texas Gulf Sulphur Company, Inc.

Fig. 61. Compressors

These produce a pressure of 500 to 600 pounds per square inch on the air which helps to mine sulfur.

Sulfuric Acid Manufacture. The manufacture of sulfuric acid is not at all a centralized process. Most of the acid is made as a subsidiary process by those industries which expect to use it in the processing of other things. In other instances the acid is produced by concerns which produce sulfur dioxide as a by-product. This and other sulfur compounds have a real money value and should be cared for anyway. It is much cheaper to convert them to sulfuric acid than it is to dump them as waste. Hence copper smelters find themselves forced to manufacture sulfuric acid. The oil refining industry needs this acid and it also must rid the crude petroleum of naturally occurring sulfur compounds. The combination of these two things results in the oil industry being in position to manufacture a part of the sulfuric acid which it needs.

Regardless of how sulfuric acid is to be made the first step in the process is the conversion of the sulfur to sulfur dioxide. If they start with pure sulfur it may be burned like any fuel. If they start with hydrogen sulfide it will also burn.

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2 + 128,000$$
 calories

Most of the copper ores are sulfides and in order to get the copper these are first heated in a blast of hot air.

$$2CuS + 3O_2 \rightarrow 2CuO + 2SO_2$$

The sulfide ores of zinc are roasted in the air in order to free them of sulfur.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

There are large supplies of iron sulfide (pyrites) which may be used as a source of sulfur dioxide by burning though they are not at present considered as ores of iron. The sulfur dioxide made from pure sulfur is free from harmful impurities while that made from burning ores is usually contaminated with impurities such as the oxides of arsenic.

The essential step in the manufacture of sulfuric acid is the union of sulfur dioxide with more oxygen to produce sulfur trioxide.

$$2SO_2 + O_2 \Leftrightarrow 2SO_3 + 45,200$$
 calories

At room temperature this reaction proceeds at an extremely slow rate. It may be caused to speed up by heating the gases but at the same time the reverse reaction by which the sulfur trioxide decomposes to oxygen and sulfur dioxide is also speeded up. There are two general methods for making the sulfur trioxide form faster than it decomposes. The first of these is to use a catalyst and the second is to use some oxidizing agent.

The Contact Process. There are several catalytic agents which will bring about the more rapid union of sulfur dioxide with oxygen. Among these are platinum, iron oxide, and vanadium pentoxide. These different catalysts do not speed up this reaction to the same extent at all. For many years a platinum catalyst was used entirely but since 1926 the vanadium pentoxide catalyst has increasingly replaced it. The impurities present in the sulfur dioxide cause a platinum catalyst to cease func-

tioning unless the gas is specially purified. It is said to become "poisoned." The makers of the vanadium pentoxide catalyst claim that it is free from such troubles.

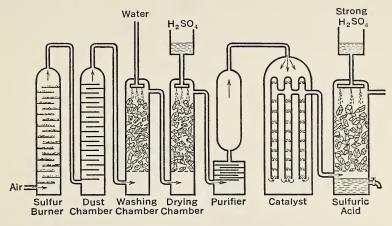


Fig. 62. The Contact Process

Let us write the reaction equation for the formation of sulfur trioxide in the reverse order to what we have done above.

$$2SO_3 + 45,200 \text{ calories} \Leftrightarrow 2SO_2 + O_2$$

From this we would infer that at high temperatures heat would be more available and as a result the sulfur trioxide would decompose. At 400° C. this decomposition is very slight but at 1000° C. it is rapid and complete. In the catalytic process it is necessary that the temperature be adjusted at some point where net formation of the sulfur trioxide is great enough to make the process possible. This occurs at about 500° C. Since a large amount of heat is liberated by the union of oxygen with sulfur dioxide it becomes necessary to cool the reaction chamber. This is done by using it as a stove to heat up the mixture of sulfur dioxide and air which is to pass over the catalyst.

The Lead Chamber Process. The process for sulfuric acid manufacture which depends upon an oxidizing agent is called the lead chamber process after the large lead-lined rooms in which the reaction takes place. In this method the sulfur dioxide from burning sulfur or metallic sulfides, together with any

impurities which it may contain, is passed into large lead-lined rooms. Into these same rooms are sent an excess of air, a mixture of nitrogen dioxide (NO₂) and nitric oxide (NO), and steam. The reactions which take place are not entirely understood but we may express the essential change as the oxidation of the sulfur dioxide to sulfur trioxide by the NO₂.

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$

The steam reacts with the SO₃ to produce sulfuric acid.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

The excess of air which is present furnishes the oxygen necessary to change the NO back to NO₂. This it does easily.

$$2NO + O_2 \rightarrow 2NO_2$$

In actual operation no sulfur trioxide is isolated and the sulfuric acid reacts with the oxides of nitrogen to form what is called "niter acid."

$$H_2SO_4 + NO + NO_2 \leftrightarrows H_2O + 2H(NO)SO_4$$
 (niter acid)

The excess of steam present decomposes this niter acid again to give the oxides of nitrogen and sulfuric acid. This, you see, is the reverse of the above reaction. Great precautions are taken to be sure that the oxides of nitrogen are not lost. The apparatus is so designed that these are all returned to the process to convert more sulfur dioxide to the trioxide.

The rooms (chambers) in which these reactions take place are huge, being sometimes as much as 150 feet long, 25 feet high, and 30 feet wide. Lead is used as their lining because it is insoluble in the dilute acid which is formed. This insolubility is due to the formation of a thin layer of insoluble lead sulfate over the surface of the lead.

The acid produced by this method contains about 63 percent of the compound H₂SO₄ in water. For many purposes this may be used without further concentration. The fertilizer industry, which is the largest single consumer of sulfuric acid, can use this dilute acid quite easily. On the other hand, the explosives

industry must have concentrated sulfuric acid which contains no water. In order to get this, either the chamber acid must be concentrated by boiling out the water, or the industry may turn to the contact process which furnishes a concentrated acid. The evaporation of the water in dilute sulfuric acid is an expensive process since costly containers must be used and

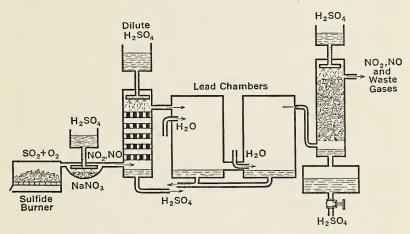


Fig. 63. The Lead Chamber Process

much heat is required. Some of the evaporation may be done in lead pans but if the acid gets stronger than 77 percent it dissolves off the protective coating of lead sulfate and the lead begins to go into solution. Sometimes porcelain, platinum, or duriron (a special alloy of iron and silicon) are used to hold the acid being concentrated.

Comparison of the Two Methods. The contact process may produce any desired dilution or concentration of acid. It is usually quite pure because the starting materials are pure. To offset these advantages is the cost of the contact process both for beginning materials and for maintenance. The catalyst must be specially prepared. If pure acid is desired the raw materials used must be pure. Both set a higher price at once. The chamber acid is furnished only in diluted form, it always contains certain impurities such as arsenic, lead, oxides of nitrogen, compounds of iron, and other metal compounds. How-

ever, the raw materials used are cheap, the upkeep of the plant is small, and the operation costs are low. The lead chamber process is able to continue in operation because a great amount of the sulfuric acid consumed may be of this dilute and impure type and thus the products sell at a lower figure. At the present time the two processes furnish almost equal quantities of the acid.

When we consider that about one third of all the sulfuric acid manufactured goes for the preparation of fertilizers, it is easily seen that a drop in farm produce prices will at once cause a drop in the amount of acid used, and thus a drop in the acid produced. It is the acid manufactured by the lead chamber process which is affected by farm conditions. Since this acid is so vital to so many different industries, the total output is directly affected by business conditions in general. A chart of sulfuric acid production shows the same variations as does a chart of business in general taken over the same interval of time. For this reason it is sometimes said that general business conditions may be predicted, or estimated, by simply observing the relative prosperity or poverty of the sulfuric acid industry. In the future this may become less true because of the growing use of hydrochloric acid in place of sulfuric. But there will be a natural limit to this substitution.

Other Uses of Sulfur. Other uses of sulfur are too numerous to list in detail here, but a few of the more common we may consider. Sulfur dioxide, which is producd by burning sulfur in oxygen, finds considerable use in the bleaching of wool, silk, and straw. When moisture is present it serves as a very effective temporary bleaching agent for these things. But in time a yellow color will appear on the goods so treated. Dried fruits are frequently exposed to sulfur dioxide to preserve the white color of the fruit, as in dried apples. But the use of cans is cutting down this use. Some effort has been made to permit the use of sulfur dioxide as a preservative for meat, but this does not appear to be safe and is at present prohibited. In the liquid form, sulfur dioxide is used to a great extent in mechanical refrigerators. The liquid evaporates in the coils within the

box and thus absorbs heat. The gas is compressed outside the box and the heat released to the air by means of a system of

cooling coils (Chapter 9).

In the manufacture of rayon by the viscose process, which is generally used, a compound of sulfur is employed. The cellulose together with sodium hydroxide is mixed with carbon disulfide (CS₂) and the viscose solution, from which the fibers are obtained, results. In the manufacture of rubber articles also it is necessary to render the rubber nonreactive to changes in temperature. This is done by heating it with sulfur in the process known as vulcanizing. Various degrees of hardness of the rubber are obtained by increasing the sulfur content of the finished product.

As an insecticide — a killer of bugs or their eggs — and fungicide — a killer of plant fungus — sulfur has many good qualities. When the very fine dust of sulfur comes into contact with many insects, it causes them to die. In the prevention of various fungus growths, such as rose spot, it is common practice to dust the plant with sulfur dust. In some instances, such as in orchards of fruit trees, it is too difficult, except by costly airplane dry-spraying to attempt dusting. Hence a solution of calcium polysulfide is sprayed onto the trees during the dormant period. The air acts upon the polysulfides to produce very fine sulfur which destroys certain of the insect pests. These solutions are known as "lime-sulfur" sprays.

Photography depends upon sodium thiosulfate (Na₂S₂O₃) which has been mentioned previously as "hypo." This substance in solution is used to dissolve out unchanged silver salts after the film or picture has been developed. The bleaching industry uses this same substance to free the bleached cloth of all excess chlorine and here it is called an "antichlor."

Sulfur is frequently used as an electric insulator for some types of electrical appliances. When molten sulfur is stirred in with sand, the mixture sets to a hard mass which makes an excellent acid-proof cement for anchoring rods in cement or stone. Sulfur is also mixed with asbestos fiber and cement to form an artificial stone which is quite resistant to chemical

action. Certain important black dyes also employ sulfur in their manufacture. And, of course as everyone knows, gunpowder and matches both must use it.

CHEMISTRY OF SULFUR

Sulfur may exist in several forms. As found in nature it is in the form of rhombic crystals. These have a density of 2.06 grams per c.c. (one cubic centimeter of it weighs 2.06 grams) and if heated rapidly will melt at 114.5° C. If the temperature is raised to a little above 96° C., however, these rhombic crystals slowly change to needlelike crystals which have a density of only 1.96 grams per c.c. and which melt at 119° C. If sulfur which has been melted is allowed to cool slowly it will solidify in the needle form. These, if cooled below 96° will slowly change to the rhombic form. Here we have another example of an element existing in more than one distinct form. It is an example of allotropy. The two kinds of crystals are allotropic forms of sulfur. The temperature at which the change from one form to another occurs is called the transition point.

Melted sulfur is a pale yellow liquid which flows as readily as water if the temperature is kept near the melting point. As the temperature is raised, the liquid sulfur becomes dark and thick (viscous). At about 200° C. it is so viscous that the tube in which it is being heated may be inverted without the sulfur running out. If the temperature is raised further the sulfur again becomes mobile and at 444.5° C. it boils. There is no doubt but that additional allotropic forms of sulfur are involved during these changes in fluidity. By pouring the almost boiling sulfur into cold water we may obtain a rubberlike mass called plastic sulfur. If sulfur is boiled and the vapors condensed on the walls of a cold vessel we may obtain a powder called flowers of sulfur.

Sulfur is Like Oxygen. Sulfur is in the same group in the periodic table as is oxygen and because of this we may expect the two elements to have certain chemical properties in common. We have seen how most of the metals will combine with

oxygen at elevated temperatures to form oxides. In the same way almost all of the metals will combine with sulfur to form sulfides. A mixture of iron filings and sulfur, if heated, will react rapidly to form iron sulfide. The heat evolved during the reaction is sufficient to heat the reacting materials to a bright red.

Fe + S
$$\rightarrow$$
 FeS (iron sulfide) + 23,000 calories

A warm piece of copper dipped into boiling sulfur becomes red-hot as the two unite to form copper sulfide.

$$Cu + S \rightarrow CuS + 11,600$$
 calories

These reactions are typical of all the metals except gold and platinum. These two metals do not react with sulfur at all.

With hydrogen, boiling sulfur unites to form hydrogen

With hydrogen, boiling sulfur unites to form hydrogen sulfide (H₂S).

$$H_2 + S \rightarrow H_2S + 5,260$$
 calories

When various compounds which contain hydrogen, such as petroleum and fats, are heated with sulfur they give up some of their hydrogen and it appears as hydrogen sulfide. This seems to be opposite to the hydrogenation process which we studied in the discussion on hydrogen.

Carbon and sulfur unite if they are heated together in closed electric furnaces. The carbon disulfide formed is extremely inflammable and must be kept away from air while it is warm.

$$C + 2S \rightarrow CS_2$$

This is a valuable solvent for rubber and is also used in the production of rayon by the viscose process. Phosphorus and sulfur unite to form P_4S_3 which is used in the heads of matches.

Sulfur Dioxide. The union of sulfur with oxygen has already been described. Sulfur dioxide dissolves in water to form sulfurous acid which is easily decomposed by boiling.

$$SO_2 + H_2O \Leftrightarrow H_2SO_3$$
 (sulfurous acid)

It is this acid which produces the bleaching action of sulfur dioxide on straw, wool, silk, and fruit which have been moistened. With alkaline substances such as sodium hydroxide and lime, sulfurous acid reacts to form salts known as sulfites.

$$2\text{NaOH} + \text{H}_2\text{SO}_3 \rightarrow \text{H}_2\text{O} + \text{Na}_2\text{SO}_3$$
 (sodium sulfite)
 $\text{Ca}(\text{OH})_2 + \text{H}_2\text{SO}_3 \rightarrow 2\text{H}_2\text{O} + \text{CaSO}_3$ (calcium sulfite)

These compounds may be formed by passing a stream of sulfur dioxide into a solution of the alkali in water. If an excess of sulfur dioxide is passed into a solution of a sulfite it produces a bisulfite due to the formation of additional sulfurous acid.

$$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$$
 (sodium bisulfite)
 $CaSO_3 + H_2O + SO_2 \rightarrow Ca(HSO_3)_2$ (calcium bisulfite)

It may be remembered that carbonic acid behaves in a similar fashion toward carbonates. Calcium bisulfite is extremely important to the paper industry because of its ability to dissolve the gluelike material (lignin) which holds the wood fibers together. Chips of wood are heated in calcium bisulfite solutions in order to separate the fibers of cellulose so that they may be used for paper. Sodium bisulfite is an excellent "antichlor" for the removal of chlorine from cloth which has been bleached.

SUMMARY

Sulfur has been known since the time of the ancients. It has long been connected with superstition and the treatment of human ills.

Compounds of sulfur occur in the cells of animals, in underground streams of water, and in the ores of metals. The free element is mined in Sicily and in Texas. Because it is so widely used it is called a key chemical.

In America sulfur is mined by the Frasch process which melts the sulfur 900 feet below the surface by means of superheated water and brings it to the surface by compressed air.

Sulfuric acid manufacture consumes a large part of the sulfur

mined. This acid is made by two methods, the contact process and the lead chamber process. The first brings about the oxidation of sulfur dioxide to the trioxide by means of air in the presence of a catalyst. The second brings about this oxidation by means of oxides of nitrogen which may react with air to be used again.

Sulfur is like oxygen in that it combines with most metals at elevated temperatures. It also combines with hydrogen and some of the nonmetals. Sulfur exists in several allotropic forms. The free element is used as an insecticide and as a fungicide. It

reacts with raw rubber to form vulcanized rubber.

Sulfur dioxide is a by-product in many industries especially in the metallurgy of the metals. It is a bleaching agent, has some preservative qualities, and is used as the liquid in some mechanical refrigerators. With water it reacts to form sulfurous acid. Sulfur dioxide is the starting point in the manufacture of sulfuric acid.

REVIEW QUESTIONS

1. Describe the Frasch process for mining sulfur. How does this differ from the method used in Europe?

2. For what reasons may we say that the consumption of sul-

furic acid is a good barometer of business?

3. From what sources may large amounts of sulfur dioxide be obtained?

4. List some uses of sulfur dioxide and state the chemical or physical change which it undergoes during each use listed.

5. What chemical change constitutes the most difficult step in the manufacture of sulfuric acid?

6. What are the relative advantages and disadvantages of the contact and lead chamber processes of making sulfuric acid?

7. What fact should make a vanadium pentoxide catalyst better than platinum in the contact process?

8. Sulfur dioxide reacts with oxygen much faster at 500° than at 200°. Why not carry out the reaction at 1000°? Explain fully.

9. What do we mean by allotropy? Transition point? Illustrate each of these with sulfur.

10. Why do we say that sulfur is like oxygen?

- 11. Of what use are: sodium bisulfite? calcium bisulfite? sodium thiosulfate?
- 12. Write the reaction equations for the preparation of calcium bisulfite from quicklime, sulfur dioxide, and water.
 - 13. List some uses for the free element sulfur.
- 14. What happens when sulfur is warmed with compounds like paraffin which contain both carbon and hydrogen?

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EXPLOSIVES, FERTILIZERS, NITRIC ACID, AMMONIA

The greatest single consumer of sulfuric acid is the fertilizer industry. Considerable sulfuric acid is also used in the manufacture of explosives, and, in the past, much has been used in making nitric acid. Because of the very close relationship between fertilizers, explosives, nitric acid, and ammonia we will discuss them in the same chapter so as to see the link connecting them. This vital relationship is due to the fact that each of

them contains nitrogen.

The Importance of Nitrogen. Nitrogen was mentioned in Chapter 4 as the chief constituent of the atmosphere of which it makes up about 78 percent. Its presence in the air is noteworthy because it dilutes the oxygen and thus prevents too rapid burning of fire and of the materials which supply heat and energy to our bodies. This property of nitrogen is typical of the great inertness of the element which shows a decided unwillingness to combine with anything else under any ordinary conditions. Nevertheless, despite this difficulty, nitrogen compounds are among the most essential for the preservation of life. The materials of which our body cells are made contain many nitrogen compounds, and it is a well-known fact that all plant and animal proteins, amino acids, and certain body regulators are nitrogen-containing substances. Another odd and important fact is that neither plants nor animals are able to draw upon free atmospheric nitrogen as a source of supply. Thus growing plants are surrounded by tons of this element, but they may starve for want of nitrogen in a usable form. The situation becomes even more pathetic when we realize that animals are entirely dependent upon plants for the source

of their nitrogen compounds. We may state the matter in a simple way by saying that plants can utilize nitrogen in the form of nitrates while animals can utilize plant or animal proteins in their various forms. The whole scheme of life, then, hinges upon the supply of nitrates in the soil.

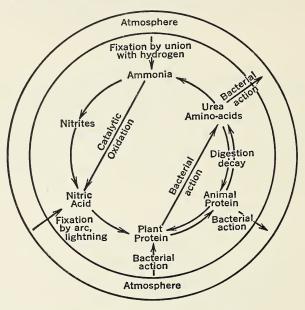


Fig. 64. Cycle of Nitrogen in Nature

The Cycle of Nitrogen in Nature. The atmosphere serves as a natural reservoir for the nitrogen supply of the world. All nitrogen-containing substances which occur in plants and animals may be decomposed by the action of bacteria, and thereby the nitrogen is released as the free element. There are certain processes which occur in nature such as lightning discharges that tend to cause the atmospheric nitrogen to unite with other elements. In addition to this there are certain manmade processes which accomplish this same result and much nitrogen is so "fixed" in the form of usable compounds. Because of the chemical combination and subsequent release of the nitrogen of the air we speak of the cycle of nitrogen in nature. The diagram of Figure 64 illustrates this idea.

Nitrogen in Explosives. Since the discovery of gunpowder, explosives have played an important part in the course of civilization. The most dramatic use of explosives is during war when battleships shell each other or towns; when airplanes drop bombs on peaceful cities; when artillery blasts at dugouts and machine guns chatter of human death. But there are many important peaceful applications of explosive power with far more lasting benefits to mankind. We have only to consider how difficult it would be without explosives to build highways, railroads, bridges, dams, mines, and tunnels in order to see that much of modern progress depends directly upon them. Now almost all explosives are made with the help of nitric acid or the nitrates which are salts of nitric acid and again we are confronted with a great demand for the same compounds of nitrogen which the plants must get from the soil.

Sources of Nitrogen Compounds. It seems a bit queer but there are very few natural minerals which contain nitrogen. In the high, desert regions of the country of Chile along the western coast of South America there is a large deposit containing sodium nitrate (NaNO₃). Until recent years this has supplied the bulk of the nitrates and nitric acid which the world has used. Naturally, such an outside source has been a serious handicap to any other country plunged in war. Just at the time when their nitrogen needs have been greatest, their certainty of supply has been at a minimum. Then, too, such a natural supply is sure to give out if worked continually. The need for some artificial source was recognized more than fifty years ago.

There is one comparatively small source of supply. The conversion of coal to coke is carried out all over the world. Coke is needed for the production of iron and other metals from their ores. This conversion of coal is accomplished by heating which drives off everything which will boil away. This includes a small amount of the nitrogen compound, ammonia (NH₃), and this substance is very carefully collected. The total ammonia obtained, of course, depends upon the amount of coke produced but it usually runs into hundreds of

thousands of tons each year. Another peculiar thing about nitrogen is that when once it is combined with other elements it is fairly easy to change it from one compound to another. Thus ammonia may be easily converted to nitric acid by well-established processes, and so the ammonia from coal finds its way into the channels of explosives and fertilizers.

Fixation of Atmospheric Nitrogen. 1. Bacteria. There are certain plants such as peas and beans, called the legumes, which

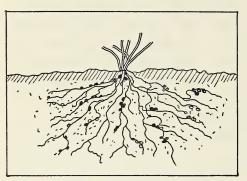


Fig. 65. Nodules of Nitrogen Fixing Organisms on Roots of Legumes

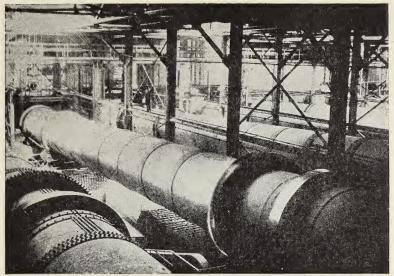
aid in the natural fixation of the nitrogen from the atmosphere. While these plants cannot react with the nitrogen their roots serve as dwelling places for a type of bacteria which do take nitrogen from the air and convert it to compounds. This process takes place at ordinary temperatures.

Surely it must not be a very difficult method of making nitrogen compounds but the secret has never been learned by man. This method of getting nitrogen into the soil is a very important one. Hence most farmers try to plant such a crop of legumes every three or four years. The nitrogen content of the plants themselves is quite high and it is common practice to "plow under" the entire crop. Some governmental aid is given to encourage the planting of legumes on poor soil.

2. Electrical Discharge. It has long been known that lightning and other electrical discharges through the air cause the union of some nitrogen with oxygen. The temperature required is about 3000° C.

 $N_2 + O_2 + 43,000$ calories \Leftrightarrow 2NO (nitric oxide)

At the temperature of the electric arc or other discharge the nitric oxide decomposes to give oxygen and nitrogen. The



Courtesy of the American Cyanamid Company

Fig. 66. Battery of Lime Kilns
Each kiln has a capacity of 100 tons of lime per 24-hour day.

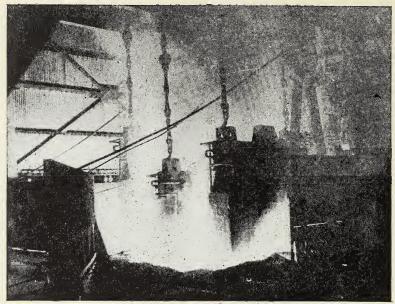
nitric oxide is able to react with additional oxygen if the temperature is much lower. In practice this may be accomplished by blowing in an excess of air.

$$2NO + O_2 \rightarrow 2NO_2$$
 (nitrogen dioxide)

The nitrogen dioxide thus produced will react rapidly with water to produce nitric acid.

$$3NO_2 + H_2O \rightarrow 2HNO_3$$
 (nitric acid) + NO

During an electrical and rain storm the nitric acid so formed finds its way into the soil but the total nitrogen fixed in this way is relatively small. As early as 1900, men tried to duplicate nature in this method by making artificial lightning. They succeeded about 1904. The amount of electrical energy required is quite high and the method can be used only with very cheap electricity. The total nitrogen so converted to



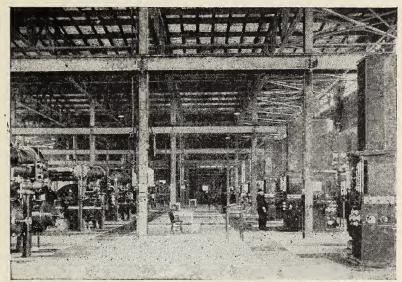
Courtesy of the American Cyanamid Company

Fig. 67. The World's Largest Electric Furnace Lime and coke are fused together at 4000° F. to produce calcium carbide.

compounds (fixed) is small and probably is used nowhere outside of Norway.

3. Cyanamide Process. During the first World War the government of the United States built a large plant at Muscle Shoals, in Alabama, which was designed to combine the nitrogen from the air with calcium carbide to form the substance known as cyanamide. The plant cost more than \$80,000,000. The process uses cheap, easily obtained raw materials and it is easily carried out. The energy consumed is quite high, though not so high as in the electrical discharge method. For various reasons the Muscle Shoals plant no longer attempts to manufacture nitrogen compounds by this method but there is at least one private company which appears to make the process pay.

The first step is the conversion of limestone to calcium oxide.



Courtesy of the American Cyanamid Company

Fig. 68. Liquid Air Plant Nitrogen is obtained from liquid air.

The calcium oxide is heated in electric furnaces with carbon to produce calcium carbide.

Next the calcium carbide is converted to calcium cyanamide by heating to 1000° in the presence of nitrogen which is obtained from liquid air.

$$CaC_2 + N_2 \rightarrow CaCN_2$$
 (calcium cyanamide) + C

The calcium cyanamide is converted to ammonia by treatment with steam under pressure.

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$$

The ammonia so produced may be converted to nitric acid.

4. Synthetic Ammonia. Of all the processes which have been proposed for the manufacture of nitrogen compounds from atmospheric nitrogen the one known as the synthetic

ammonia, or Haber, process is the most successful. This involves the direct union of nitrogen and hydrogen to form ammonia.

$$3H_2 + N_2 \Leftrightarrow 2NH_3 + 24,000$$
 calories

At room temperature nitrogen and hydrogen appear to react not at all. At 550° C. and at atmospheric pressure it is possible to get 0.08 percent of the mixture to react and form ammonia. Any larger amounts of ammonia present are decomposed to nitrogen and hydrogen. We say that the equilibrium is reached with this amount of ammonia. Without a catalyst the rate of formation of ammonia at this temperature is extremely slow. At 1000° ammonia is completely decomposed to the elements. This means that the temperature must be kept low enough to prevent the decomposition and yet high enough to give some ammonia. Haber applied a little reasoning to the reaction and solved the problem. If you will look at the reaction equation you will see that three molecules of hydrogen and one molecule of nitrogen react to give two molecules of ammonia. From the law of Avogadro you will recall that there should be a decrease in volume as this change takes place. The volume of ammonia should be only half of the volume of the two reacting gases combined. Haber reasoned that an increase in pressure should favor the smaller volume. In like manner an increase in temperature supplies more heat and the reverse reaction is encouraged. By increasing the pressure to about 3000 pounds per square inch and keeping the temperature at about 550° Haber was able to get about 8 percent of the gas mixture converted to ammonia.

In order to speed up the reaction it is customary to use a catalyst. The most successful of these are those which contain the oxides of iron, potassium, and aluminum. It is necessary that the catalyst last a long time and that it be free from danger of being poisoned.

The nitrogen is obtained from liquid air and the hydrogen is obtained by passing hot steam over burning coke or by the electrolysis of water. The pure gases are mixed in the proper

proportions, heated, and passed over the hot catalyst. The ammonia produced is removed by permitting it to react with a suitable reagent and the unreacted gases are returned to the process.

Comparison of the Methods. As in other things, the availability and costs of energy and materials have determined the

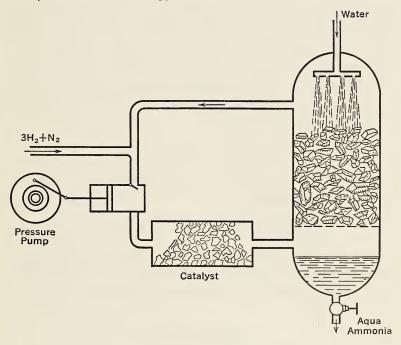


Fig. 69. Synthesis of Ammonia

relative importance of the various processes discussed. This will be obvious when the facts are considered. To fix a ton of nitrogen (convert a ton of the element to its compounds) requires 4000 kilowatt hours of energy if done by the Haber process, 15,000 kilowatt hours if done by the cyanamide process, and 65,000 kilowatt hours if done by the electrical discharge process. Such a wide difference cannot be overlooked. These figures alone give sufficient reason for the rapid conversion of all nitrogen fixation plants so that they will operate by the synthetic ammonia process.

Production of Nitric Acid. Until the production of synthetic ammonia became world wide, most of the nitric acid used was prepared by treating sodium nitrate, from Chile, with sulfuric acid.

$$H_2SO_4 + NaNO_3 \rightarrow NaHSO_4 + HNO_3$$

The mixture was heated and the more volatile nitric acid boiled off. At the present time, however, there is very little nitric acid produced in this manner because synthetic ammonia may be converted to nitric acid cheaply enough to compete successfully. When ammonia and air are passed over a hot catalyst of platinum gauze the ammonia is burned to nitrogen dioxide and water.

$$4NH_3 + 7O_2 \rightarrow 4NO_2 + 6H_2O$$

In the presence of water the nitrogen dioxide is converted to nitric acid quite rapidly.

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

The method is successful and the acid so produced is quite pure and of any desired concentration. The ammonia for the manufacture of nitric acid may come from any suitable source.

EXPLOSIVES

Most of the nitric acid produced is used in the manufacture of explosives. A number of compounds containing carbon and hydrogen will react with nitric acid to form substances which under certain conditions decompose with immense speed and form large volumes of gaseous products. Usually the gases produced consist of carbon monoxide, carbon dioxide, nitrogen, oxygen, and steam. Frequently the rate of decomposition is so rapid, and the heat evolved is so great, that an expansion of 100,000 times the original volume takes place almost instantly. Such an increase in volume results in tremendous pressure which blows outward. The result we call an explosion.

Nitroglycerin and Dynamite. Nitroglycerin is formed by the treatment of glycerin with a mixture of concentrated nitric and sulfuric acids.

$$C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(NO_3)_3 + 3H_2O$$

The nitric acid reacts with the hydroxyl (OH) groups of the glycerin to form glyceryl nitrate and water. The concentrated sulfuric acid reacts with the water and prevents it from diluting the nitric acid. The glyceryl nitrate is called nitroglycerin. It is quite sensitive to both shock and heat though is much used in oil field practice.

Nitroglycerin is not safe to handle. But if it is absorbed in some inert material, such as sawdust or wood flour, its sensitivity to shock is considerably lowered. Such a mixture is found in dynamite which is wood flour mixed with nitroglycerin and packed in cylinders of waxed paper. The material is caused to explode by means of a detonating cap which, in turn, is set off by fire from a fuse or electric spark. The development of dynamite and many similar explosives resulted from the studies and experiments of the Swedish chemist, Alfred Nobel, who later set aside a considerable sum of money to endow the international prizes which bear his name.

Nitrocellulose. Nitric acid acts upon cellulose and starch in a manner which is entirely similar to its action with glycerin. These two substances contain hydroxyl groups (OH) in their molecules and nitric acid replaces such groups by nitrate groups (NO₃). Both cellulose and starch may be represented by the formula (C₆H₁₀O₅)_x which means that they each contain carbon, hydrogen, and oxygen in the ratio shown but the actual molecule is many times the simple formula. Just how many times the simple formula must be used to represent the actual formula we do not know and so we write the subscript "x." We may also write this formula so as to show the hydroxyl groups, and, by so doing, show its reaction with nitric acid.

$$(C_6H_7O_2(OH)_3)_2 + 6HNO_3 \rightarrow C_{12}H_{14}O_4(NO_3)_6 + 6H_2O_3$$

The water formed is removed by means of concentrated sulfuric acid as in the nitration of glycerin. The nitrated product is known as *guncotton* and finds considerable use in the manufacture of "smokeless powder."

If the action of the nitric acid is stopped after three or four of the nitrate groups are introduced the product is nonexplosive and is called "pyroxylin." This substance is used as the basis for the production of lacquers, artificial leather, pho-

tographic film, and pyralin.

Nitrotoluene and Nitrophenol. With certain organic liquids such as toluene (C₇H₈) and phenol (C₆H₅OH) nitric acid acts in a slightly different manner to produce explosive substances. Instead of replacing hydroxyl groups by nitrate groups it is found that hydrogens have been replaced by nitro groups (NO₂).

$$\begin{array}{c} C_7H_8 \,+\, 3HNO_3 \rightarrow C_7H_5(NO_2)_3 \,+\, 3H_2O \\ \text{toluene} & \text{trinitrotoluene (T.N.T.)} \\ \\ C_6H_5OH \,+\, 3HNO_3 \rightarrow C_6H_2(NO_2)_3OH \,+\, 3H_2O \\ \text{phenol} & \text{trinitrophenol (picric acid)} \end{array}$$

In each case the water formed is removed by concentrated sulfuric acid. Both of the nitro compounds mentioned are high explosives if they are properly used but may be handled with perfect safety. Picric acid (trinitrophenol) is also an important yellow dye. It is, in addition, widely used by medicine in the treatment of burns and is a basic material for some sunburn salves.

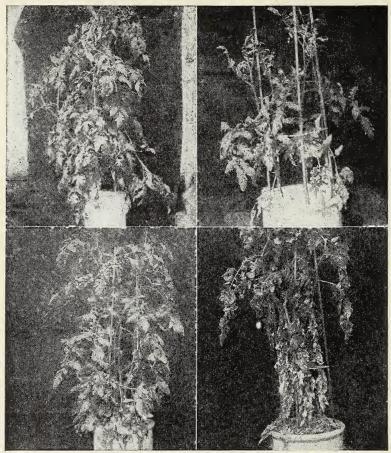
Black Powder (Gunpowder). The discovery of gunpowder dates back many centuries. It has been attributed to the Chinese, to Bacon in England, and to various other sources. However, the essential ingredients are always the same. Carbon and sulfur are mixed with a nitrate, usually potassium nitrate. During the burning, the nitrate (KNO₃) furnishes the oxygen to burn the carbon and sulfur so that large volumes of gas are produced. The rate of gas formation, however, is much slower than with such explosives as nitroglycerin and guncotton, and, as a result, the shock due to the explosion is less severe.

In the mining of coal and quarrying of building stone the explosive is used to loosen the material but must not shatter it. This calls for black powder rather than for dynamite. In actual mining practice many factors must be considered and much research has been done in an effort to prevent fires due to the flash of the explosive. Most explosive companies have developed special types of explosives for coal mining in particular so as not to fire the gases ("damp") nor the dust in the still air.

There are quite a number of companies who manufacture nothing but industrial explosives. Some idea of the size of the industry can be obtained from the fact that in 1936 it produced 392,000,000 pounds of industrial explosives.

FERTILIZERS

The growth of plants seems to be such a simple thing. We have been told for many years that the plant absorbs carbon dioxide from the air, drinks in water from the soil, and, under the influence of the rays of the sun in the presence of the green chlorophyll, produces new plant tissue. We may be tempted to believe that nothing else is required. Experience has shown, however, that the process is really much more complex and that under certain combinations of plant food, soil chemistry, sunlight, temperature, and moisture plants will grow huge root systems and stunted puny tops. Under others they will go all to stem and leaf. Under still others they will develop perfect flowers or seeds. The early American settlers, for example, learned from the practical Indians that better corn resulted if two or three fish were planted beneath each corn stalk. Of course, some sections of the world are so situated geographically that the combinations are about right for what they grow and they do not need to give any thought to the requirements for plant food. But the great majority of the farmers and growers of the world have been through the centuries thinking and crudely experimenting to find ways to get better plants by giving them better food and drink.



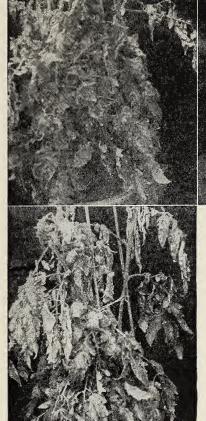
From Maryland Experimental Station Bulletin No. 375

Figs. 70-73. The Effect of Nitrogen, Phosphorus, and Potassium on Plant Growth

Tomato plant with complete fertilizer (70), lacking nitrogen (71), lacking phosphorus (72), lacking potassium (73).

Photographs supplied through the courtesy of Dr. Paul L. Fisher, Chairman, Botany Department, Riverside (Cal.) Junior College

Plant Food. An analysis of plant tissues gives some idea of the elements which are necessary for the growth of plants. Such study also indicates the amounts of the required elements which are removed from the soil by growing crops. However, the relative abundance of these elements in the plant tissue does not indicate the true importance of the elements.





From Maryland Experimental Station Bulletin No. 375

Figs. 74–76. Effect of Minor Elements on Plant Growth

Tomato plants treated like that in Figure 70 except that calcium is absent (74), magnesium is absent (75), boron is absent (76).

Photographs supplied through the courtesy of Dr. Paul L. Fisher, Chairman, Botany Department, Riverside (Cal.) Junior College

Thus one element may be present in mere traces in the plant but its complete absence from the soil in which the plant grows may cause its growth to all but cease. In general, the required elements are listed under two main divisions. The first contains those which are required in large amounts and which are removed from the soil to a considerable extent. These are called the elements for *primary* plant requirements and they are nitrogen, potassium, and phosphorus. Nitrogen promotes the formation of foliage; potassium aids in the formation of roots and seeds and contributes to the general health of the plant; and phosphorus makes for more sturdy stalks. In actual prac-



From New Jersey Station Bulletin No. 603

Figs. 77-78. Effect of Boron on Cotton Plant

Plant with well formed bolls fed on complete fertilizer (77). Similar plant given all required fertilizer elements except boron (78). Bolls have dropped off as soon as formed.

Photographs supplied through the courtesy of Dr. C. H. Wadleigh, University of Arkansas

tice there is a certain required balance between these three elements and for this reason they are spoken of as the "Agricultural Triad." The second division of required elements are called *secondary* plant requirements. The amounts of these which are removed from the soil by growing plants are small, but their presence appears to be quite necessary. These are further divided into two groups: those which must be present in rather large amounts; and those which need to be present only in traces. Under the first group we find calcium, sulfur, and magnesium while under the second we find iron, copper, manganese, zinc, and boron. These last are usually present in the soil in sufficient amounts to care for the needs of the plant.

The functions of the various required elements are not fully known, but we can hazard guesses about some of them. Nitrogen and phosphorus appear in the plant tissue. But it seems that potassium does not take part in the organic compounds

formed. Calcium seems to enable the plant to make the best use of the water available and aids in the assimilation of the other required elements. Magnesium is present in the chlorophyll molecule, but iron appears to be necessary to the forma-tion of chlorophyll. The other elements surely perform some catalytic function which we do not understand at this time. In the light of recent findings it appears that any plant is a complex chemical laboratory to which one supplies certain raw materials and from which one may obtain various useful plant tissues. One may conclude that the soil itself is unnecessary except as a support for the roots so long as all the necessary foods are present. It is interesting to note that there are just now emerging many ardent gardeners who are happily growing vigorous plants which produce enormous yields of fruit when their gardens consist of nothing but water tanks containing dilute solutions of the required elements. Metal or wood screens, sand or other suitable porous material is used merely to support the roots of the plants in the chemical bath.

The Fertilizer Industry. Because of the great need for fertilizer materials, there has grown up a large industry which attempts to meet these requirements. All over the country there are large and small mixing plants which gather in raw material having a fertilizer value, mix these in different proportions for different purposes, and then sell the mixtures to the farmers. Usually these mixtures are sold with the percentage of nitrogen, phosphorus and potassium specified in terms of nitrogen, phosphorus pentoxide (P₂O₅) and potash (K₂O) which is potassium oxide. In addition to compounds of these three elements most fertilizer mixtures contain small amounts of those other ingredients which meet the secondary plant food requirement. In 1937 there were in the United States more than 700 mixing plants which manufactured mixtures with a sale value of about \$200,000,000.

Sources of Fertilizer Material. To meet the demands of such a large industry there must be an abundant supply of raw material, and this has brought about an extensive investigation of our natural resources.

- 1. Nitrogen Sources. The source of nitrogen compounds has been fully discussed earlier in this chapter. The fertilizer industry consumes large amounts of ammonia in the form of ammonium sulfate. When applied to the soil, the ammonia present is oxidized, with the aid of the air and bacteria, to nitrates which the plant can use. Other nitrogen compounds used include calcium cyanamide, calcium nitrate, Chilean nitrate, and various plant wastes such as rotted leaves and straw and animal waste such as ordinary manure, and the ground bones and other discards from the packing houses, which may be rich in nitrogen compounds. The present nitrogen fixing industry is certainly well able to care for all the needs which may arise, and we should have no fear of ever running out of compounds of this valuable element. In 1937 the entire world was prepared to manufacture nitrogen compounds equivalent to 3,763,000 tons of nitrogen each year, which in addition to ammonia from coal and the natural sources of nitrogen amounts to a tremendous quantity which is far more than the agricultural needs. In this material and manufacture the United States is exceeded only by Germany and Japan. Our own industries for the fixation of nitrogen will surely be expanded to a great extent as a means of defense.
- 2. Phosphorus Sources. There are extensive natural deposits of phosphorus compounds in this country as well as in various other parts of the world. Our sources have been deposits of impure calcium phosphate, known as "rock phosphate," which occur in Tennessee, Florida, and South Carolina. But recent developments have shown an almost unbelievable amount of such material in the Western states of Montana, Idaho, Wyoming, and Utah. It is easier to get at the deposits in the eastern part of the country and transport the mined material to market. Hence these are being worked the most. The total reserves of this material run to about 6.5 billion long tons so that we cannot possibly see a shortage at any future time.

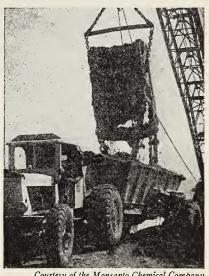
The rock phosphate as it comes raw from the ground cannot be utilized by growing plants because the phosphate is relatively insoluble in the water of the soil. In order to increase the solubility of the phosphorus content of the rock, it is treated with acid which converts it to the so-called superphosphate. Sulfuric acid is usually employed.

$$\begin{array}{c} Ca_3(\mathrm{PO_4})_2 \,+\, 2H_2\mathrm{SO_4} \longrightarrow Ca(H_2\mathrm{PO_4})_2 \,+\, Ca\mathrm{SO_4} \\ \text{rock phosphate} \end{array}$$

The superphosphate is available for plant food as soon as it enters the soil because it is readily soluble in water. There is

one serious objection to such a material, however, as it contains many things which are not really plant food. It is true that the calcium and sulfur have a place as constituents of fertilizer material but as far as phosphorus is concerned the content of this element in the mixture is quite low (16 to 20 percent P_2O_5). If the fertilizer must be shipped very far, the freight on the unwanted material becomes excessive.

Recent Trends. Modern developments in the utilization of electrical energy have made possible the new production of phosphoric acid in consid-



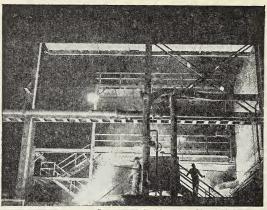
Courtesy of the Monsanto Chemical Company

Fig. 79. Loading Phosphate Rock from Open Pit Mines in Tennessee

The phosphate is transported to the sintering plant and the electric furnaces.

erable amounts. If the rock phosphate is treated with this acid it produces a soluble superphosphate with the absence of calcium sulfate. Some of the material so produced may contain as much as 70 percent P₂O₅ and is an extremely concentrated fertilizer. The production of cheap electricity by the T.V.A. has given new life to this industry and already several commercial firms are making such products.

The chemical changes involved in the production of phos-



Courtesy of the Monsanto Chemical Company

Fig. 80. Tapping Electric Elemental Phosphorus Furnaces for Slag and Ferrophosphorus

Monsanto, Tennessee plant of Monsanto Chemical Company.

phoric acid are fairly simple. The phosphate rock, carbon in the form of coke, and sand are placed in an electrically heated furnace.

$$\begin{array}{c} Ca_3(PO_4)_2 \,+\, 3SiO_2 \rightarrow 3CaSiO_3 \,+\, P_2O_5 \\ P_2O_5 \,+\, 5C \quad \rightarrow 2P \quad \, +\, 5CO \end{array}$$

The phosphorus vapors are burned in air and changed back to the oxide.

$$4P\,+\,5O_2\rightarrow 2P_2O_5$$

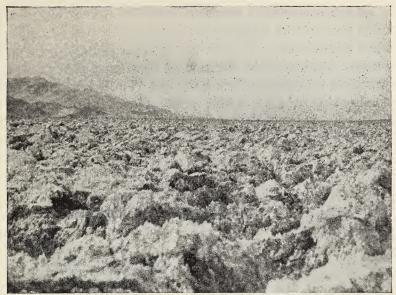
The oxide is dissolved in water to produce an acid of any concentration desired.

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$
 (phosphoric acid)

With rock phosphate this acid produces the soluble calcium acid phosphate (superphosphate).

$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2$$

At the present time there is a practice of condensing the vapors of phosphorus as they come from the electric furnace. They then ship the element phosphorus to the fertilizer plant where



Photograph by M. S. MacLean, Jr.

Fig. 81. The Sponge-like Surface of the Salt Beds in Death Valley

it may be burned and converted to the acid. A considerable saving of freight costs is thus effected.

Some idea of the size of the phosphorus and phosphate industry may be obtained by a glance at figures. In 1937 almost a million tons of phosphorus as phosphorus pentoxide was utilized in the United States. Of this, almost 84 percent went into fertilizers. The total consumption of phosphate rock in 1937 was more than 3.25 million tons in this country alone.

Potassium Sources. When the early American settlers saved all of the wood ashes and treated them with water it was for the purpose of obtaining the much needed potassium salts which they contained. Ordinarily the potassium was present as the carbonate or the hydroxide, and, because of this, the solution was quite alkaline. While the solution was their chief source of alkali for soap, its principal ingredient was also essential for gunpowder. As a result of this primitive method for getting potassium compounds the name "Potash" has been generally applied to potassium salts of all kinds.

As the agricultural needs for potash became recognized other sources were sought. For many years the world depended upon a natural deposit which occurs in parts of Germany and France. The particular location of these important minerals was quite unfortunate during the first World War, since this conflict shut off the available supply. Hence it became neces-



Courtesy of the American Potash and Chemical Corporation

Fig. 82. The Surface of Searles Lake

sary for the rest of the world either to find other sources or do without potash. In the United States some potassium salts were obtained from wood ashes, ashes from seaweed, scourings from wool, dust from cement kilns, and waste sugar molasses. However, all of these together did not furnish anywhere near enough potash to begin to supply the demand.

Within fairly recent years a considerable amount of prospecting for potash has been going on, and large amounts of potassium compounds have

been discovered in such widely separated areas as Russia, Poland, Spain, and the United States. The discoveries in the United States have come largely through the efforts of various governmental agencies and after many years of seemingly futile effort. An old dried lake bed in California, known as Searles Lake, first came into production. This was followed by a discovery in New Mexico which began production in 1931. The New Mexico deposits occur about 1000 feet beneath the surface and were discovered while drillings were being made for oil. This field has increased its output to about 500,000 tons of potassium chloride per year. At the present time it seems as

if there are enough reserve potassium minerals "in sight" to

furnish all the potash required for many centuries.

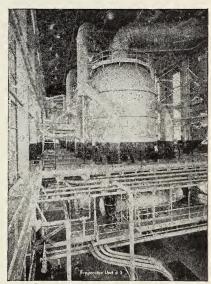
There are many uses for potassium compounds other than for fertilizers but most of the production goes to the soil. In a normal year the United States consumes the equivalent of more than 350,000 tons of potassium oxide (K₂O) which contains a much higher percentage of the element than do the various salts.

SUMMARY

Nitrogen is an essential element for explosives and fertilizer. It is characterized by its unwillingness to take part in chemical

reactions as well as by the instability of the compounds which it does form. Living cells contain nitrogen compounds which are essential to life. Plants utilize nitrogen in the form of nitrates from the soil. Animals may use plant or animal proteins. The life process tends to return all nitrogen, contained in its compounds, to the air as the free element.

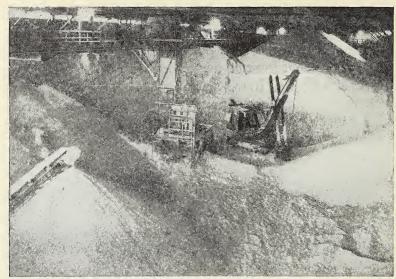
Nitrogen from the air is made to combine with other elements by means of violent electric sparks through air, by reaction with calcium carbide at a



Courtesy of the American Potash and Chemical Corporation

Fig. 83. Evaporator for Recovery of Salts from Searles Lake

high temperature, and by the union with hydrogen under pressure in the presence of a catalyst. This union with hydrogen is the most successful method. Nature tends to fix some nitrogen by means of lightning discharges through the air and by means of bacteria which live on the roots of legumes.



Courtesy of the American Potash and Chemical Corporation

Fig. 84. Potash Storage Bin

Ammonia is obtained as a by-product in the manufacture of coke from coal. Sodium nitrate is found in Chile and from it nitric acid may be made. Ammonia may be converted to nitric acid.

Explosives are compounds of nitrogen made from nitric acid. The rapid decomposition of these compounds produces suddenly large volumes of gas which causes the explosion. The common explosives are nitroglycerin and dynamite, nitrocellulose or guncotton, nitrotoluene or T.N.T., nitrophenol or picric acid, and gunpowder. Various explosives are modifications of these.

The primary fertilizer elements are nitrogen, phosphorus, and potassium. The secondary fertilizer elements are calcium, sulfur, magnesium, iron, copper, manganese, zinc, and boron. Some of these take part in plant tissue formation while others appear to act as catalysts.

Our sources of fertilizer elements are ample to supply all of our needs. Plants for the manufacture of synthetic ammonia are well established. Phosphorus is found abundantly as calcium phosphate. Potassium is found as potassium chloride in California and New Mexico.

For fertilizer use we may employ salts of ammonia or it may be changed to nitric acid and then to nitrates. Phosphorus must be in a soluble form. This is accomplished by treating the calcium phosphate with sulfuric acid. New methods convert some of the calcium phosphate to phosphorus. The latter is burned, changed to phosphoric acid, and this acid used in place of sulfuric acid with calcium phosphate. Potassium may be applied as the chloride or sulfate.

REVIEW QUESTIONS

- 1. In what form must nitrogen be for the use of plants? Of animals?
 - 2. What do we mean by the cycle of nitrogen in nature?
 - 3. List the chief sources of the compounds of nitrogen.
- 4. Why is the electrical discharge method of nitrogen fixation not more used?
- 5. Describe the Haber process. Why is the reaction favored by an increase in pressure? Why must the temperature be controlled?
- 6. Compare the chemical changes involved in the production of nitric acid by the electrical discharge method with those involved in its production by way of the Haber process.
- 7. Compare the synthetic ammonia process with the calcium cyanamide process as regards the product and energy required.
- 8. List the more important explosives. From what are they made?
- 9. What is the relation of dynamite to nitroglycerin? Who discovered it?
- 10. In what way does the formation of guncotton differ from the formation of T.N.T.?
 - 11. What are the requirements for a high explosive?
- 12. What kind of explosives are best for coal mining? For rock quarrying?
 - 13. List the primary and secondary plant food elements.
- 14. Give the sources of nitrogen, potassium, and phosphorus compounds for agricultural use.

15. What is superphosphate? What are its advantages over ordinary calcium phosphate?

16. How has cheap electricity affected phosphate fertilizers?

17. Why is the use of phosphoric acid better for the production of superphosphate than the use of sulfuric acid for the same purpose?

18. Why should potassium ammonium phosphate (K(NH₄)₂

PO₄) be an ideal fertilizer to ship and apply?

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METALS

The metallic elements make up a most important group of our natural resources. The uses to which various metals are put are so generally well known to us that it will not be necessary to dwell at length upon them. No one knows within thousands of years when iron, copper, gold, silver, lead, mercury, and tin were first used because it all happened before men made written records of their activities. But down through the ages, these metals have been vastly important to men for their weapons of war, their tools in peace, and for decoration and adornment of themselves for pride and pomp or of their places of worship of whatever gods they held in reverence.

In the modern world the dependence of industry in general upon iron is reflected by the close agreement between iron production and financial prosperity of the world. Present-day use of electrical energy has brought about the production of enormous quantities of a very pure copper which has an exceptional electrical conductivity and carries our light, power, voices, photographs in seconds of time. The extreme lightness of aluminum, together with its great strength, has made us able to fly in swifter, stronger airplanes; lighten the weight, step up the speed and increase the economy of our other machines in which lightness must be combined with strength. Because it forms desirable alloys with aluminum, we now find large amounts of magnesium going into these same fields.

There are many other metallic elements which find lesser gross use but which are nevertheless just as important as those mentioned. Some of these were known only in museum collections just a few years ago. Now we have steels containing varying amounts of such metals as nickel, chromium, man-

ganese, vanadium, tungsten, and molybdenum which are noted for the special properties imparted to the steel by very small amounts of the added elements. These steels are mostly iron with a little carbon, and contain sometimes as little as one tenth of one percent of the added metal. Such alloys have properties such as unusual toughness, hardness, resistance to wear, resistance to stain, resistance to rusting, and resistance to fatigue. There is also the great and growing field of metallic coatings where we find iron plated, or otherwise covered, with such elements as zinc, nickel, tin, and chromium. These either tend to prevent rusting of the iron or present a permanently shiny and good-looking surface.

Ores. There are certain metals that tend to resist chemical action, and such metals are usually found free in nature. It has been pointed out that gold, silver, and copper were used even before the dawn of history. This was probably true just because they were attractive bits of semiplastic material which satisfied a desire for ornamentation. After men discovered that objects made of such stuff were very durable it was natural that they used these metals to fashion useful things. Such metals which occur free in nature are said to be *native*. In addition to those mentioned there are several others which occur

native, chief of which are platinum and mercury.

Most of the metals are found in the earth in the form of various compounds. Of these there are a few which have greater industrial importance than do others. Large amounts of iron, aluminum, zinc, tin, and copper are dug from the earth in the form of their oxides. Lead, zinc, antimony, copper, and bismuth are found in the form of their sulfides, while sodium and potassium exist chiefly as the chlorides. In many cases rather large amounts of certain metals are found in the form of their carbonates. This is particularly true with calcium and magnesium, but some important supplies of iron are also in this form.

There are many metallic compounds in nature which do not lend themselves to the production of the free metal even though they are abundant. Thus clay contains considerable aluminum, but no way has yet been devised for the satisfactory production of aluminum from this source. The sulfide of iron is also common, but this fails as yet to serve as a usable source of iron. All of these things which are found in the earth are called *minerals* but *only those which serve for the profitable production of the metals are spoken of as ores*.

Metallurgy. The extraction of the metals from their ores is termed metallurgy. To a certain extent all of the metals are obtained by very similar processes. These general methods are usually referred to as the principles of metallurgy, and a fair knowledge of the entire field may be obtained by a con-

sideration of these. Briefly, they are as follows:

1. Concentration of the Ore. As a general rule, the ore is not at all pure but is mixed with a considerable amount of rock and dirt which must be removed before the metal can be extracted profitably. Sometimes such concentration may be brought about by picking the rocks out of the ore, or a stream of water may wash away the lighter dirt and stone. In many cases the rock and ore are crushed together and treated with water mixed with a certain oil. Violent agitation of the mixture with air will cause the ore to float to the top, and thus is brought about a very effective concentration. Such a method has been applied to a number of ores and is known as the flotation process.

2. Roasting. If the concentrated ore is an oxide it may be heated with carbon which combines with the oxygen to leave the metal. But not all the ores are oxides. Many of the ores may be converted to the oxides, however, by heating in a furnace in contact with large amounts of fresh air. This process is called roasting. It may be applied to most of the metallic sulfides which burn to form the oxides and the gas sulfur dioxide; and to the carbonates which decompose to form the oxides and the gas carbon dioxide. A great amount of zinc ore in the form of the sulfides is so roasted and the oxide obtained. The same principle is applied to copper sulfide ores, but these are much more difficult to handle and the change is never complete.

3. Reduction. If the metallic element concerned is not too active chemically, the oxide may be changed to the metal by heating it with carbon. But with very active metals other methods must be used. Thus the oxides of iron, copper, zinc, and tin are reduced by hot carbon. Aluminum, magnesium,

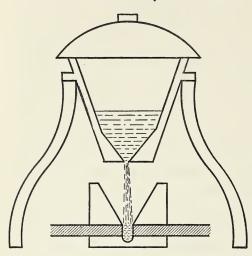


Fig. 85. Thermite Crucible in Place to Weld Rail

sodium, and potassium cannot be so prepared. It is a simple case of the carbon and the metal fighting with each other for the oxygen, and, if the metal is the more active, the carbon cannot take the oxygen away.

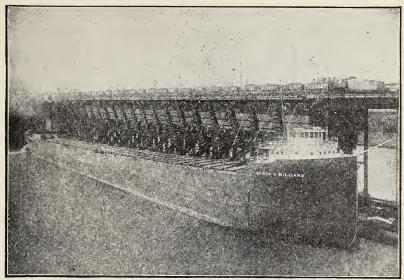
Certain elements which cannot be released from their oxides by means of carbon may be obtained by heating the oxide with powdered aluminum.

The aluminum is so very active that it combines with the oxygen with great rapidity and evolves large amounts of heat. The resulting metal is naturally expensive; and the method is employed only in exceptional cases. The best example of this method is observed in the welding of streetcar rails. A crucible charged with iron oxide and aluminum powder (the mixture is called thermite) is placed over the rail and ignited by means of a piece of burning magnesium.

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe + heat$$

The heat produced keeps the iron melted and this is allowed to run into a mold placed at the sides of the rails to be welded. The ends of the rails melt and together with the added metal they become one continuous rail.

4. Electrical Reduction. One of the more important meth-



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Fig. 86. Loading an Ore Boat

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ods of reduction employs an electric current. Sometimes a melted compound of the metal will conduct electricity and in such cases the metal will deposit out on the negatively charged electrode. It is in this manner that sodium and magnesium are produced from their melted chlorides. In other cases it is necessary to dissolve the metallic oxide in a molten mixture which will conduct the current. Thus it is that aluminum is produced by passing electricity through a mixture of purified aluminum oxide dissolved in molten cryolite. The cryolite is a compound of aluminum (Na₃AlF₆) which when melted conducts the electric current.

5. Purification. After the usual process of reduction the metal so obtained is never pure and must be further purified before use. Of course, aluminum and other metals produced by electrical means are usually pure. The purification process is quite varied. The impurities to be removed as well as the metal in question determine the procedure, and no general method can be employed for all. With iron the impurities are

burned out, while with copper the metal is dissolved in acid and then plated out by means of electricity.

Metallurgy of Iron. The production of iron from its ore is probably more interesting than that of any other metal. It is by far the most widely used metal and in its metallurgy we find examples of each of the steps which have been outlined.

The largest deposits of iron ore in the world are found in the Lake Superior region in the United States near Marquette, Michigan, and Duluth, Minnesota. These beds of hematite (Fe₂O₃) have already supplied more than 1,500,000,000 tons of ore and they still contain far more than this amount. Some of the ore is found very near the surface where it is mined in open pits, but much of it occurs deep in the ground where it is reached from shafts. During the mining of the ore, a reasonable amount of care is exercised in order that nothing but ore will be taken from the mine. Since the ore bed is quite consistently uniform in composition, this results in the handling of ore which is relatively high-grade. The chief impurities consist of silicates and other substances which are difficult to remove by mechanical means.

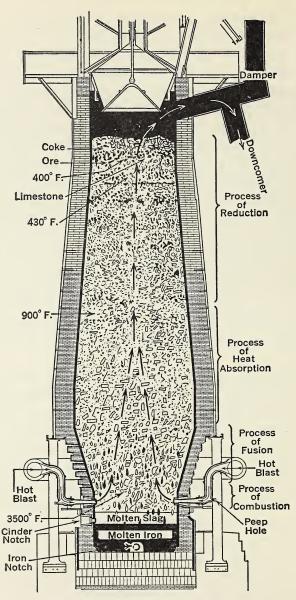
Reduction of the Ore. In order to convert iron oxide to iron it is only necessary to heat the oxide with carbon. However, for every two tons of ore used it is necessary to use one ton of carbon in the form of coke. Most of the ores contain acidic impurities such as silicates and phosphates, and it is possible to remove much of these very simply during the reduction. It may be recalled that, during the manufacture of glass, the furnace charge contains limestone and sand which react to form the easily melted calcium silicate.

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$$

By the use of limestone during the reduction of iron ore, it is possible to convert the impurities into just such a glasslike substance as is made in the glass furnace. It is true that other impurities present in the ore will also appear in this glass and as such it has no value. This resulting material is called *slag* which finds some use in the manufacture of cement.

Location of Cities. It may be seen that the production of iron requires ore, coke, limestone, and air. Naturally there is a transportation problem involved with three of these substances and we find them meeting near the coal supplies. It is much easier to transport the ore, heavy as it is, without damaging it, than the bulky coke which crumbles on handling. The ore may be shipped by water at little expense. In former years the ore was shipped by rail from the lake ports to the coke plants, but manufacturers have increasingly been shipping coal to the port where the ore is landed and there produce the coke. In many instances the ore boats are now able to unload their cargo directly in the yard of the reduction plant (Buffalo, Cleveland, Detroit, Gary, Chicago). The limestone needed may usually be found somewhat nearer than the other materials. In Alabama, particularly at Birmingham, the ore and the coal occur very near each other and not far away is an ample supply of limestone. It is not difficult to understand, in the light of such economic factors, why certain industrial centers have come to be great iron and steel producers. Around such centers cities develop.

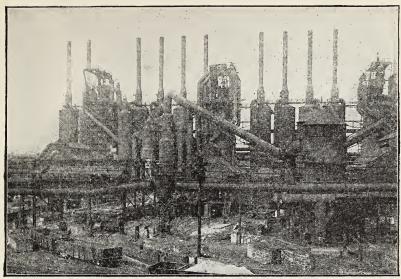
The Blast Furnace. Iron ore is reduced in a special furnace known as the blast furnace. This is a huge chimneylike affair which may be nearly 100 feet high and as much as 25 feet in diameter. The ore, coke, and limestone are fed into the top of the furnace through a double trap door which keeps the opening closed during the entrance of the charge. Near the bottom of the furnace there is a series of pipes through which hot air is blown into the furnace. At this point the coke burns with the evolution of a great amount of heat, and the hot gases proceed upward through the ore and coke. The molten iron, together with molten slag, drip down to the bottom of the furnace where a special crucible serves for their collection. The slag floats on top of the iron, and each may be drawn off separately as often as necessary. The exhaust gas from the furnace is not only hot, but there is a considerable amount of carbon monoxide present in it. This gas mixture is burned in stoves and serves to heat up the air which is to be used for the blast. The



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Fig. 87. Section of a Blast Furnace

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Fig. 88. Blast Furnaces and Stoves

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excess furnace gas is used as a source of power to run the machinery of the plant.

Interesting chemical changes occur in the blast furnace. At the point where the hot air enters, the coke burns rapidly to produce carbon dioxide, and the temperature reaches 2000° C.

$$C + O_2 \rightarrow CO_2 + heat$$

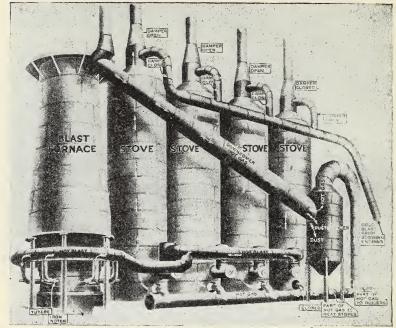
All of the oxygen is soon used as the air travels upward, and the hot coke is completely surrounded with carbon dioxide. At the temperature attained, the hot coke reduces the carbon dioxide to carbon monoxide.

$$C + CO_2 \rightarrow 2CO$$

As the hot carbon monoxide travels upward it strikes the hot ore which it reduces to iron.

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

The molten iron drips steadily toward the bottom. The molten slag dripping with the iron serves as a liquid in which the small



From An Introduction to Chemistry, by J. A. Timm

Fig. 89. How the Blast is Heated

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drops of iron may collect easily and form streams which then flow downward rapidly.

The iron produced by the blast furnace is not pure. It contains between 2 and 4.5 percent carbon, up to 0.1 percent phosphorus, from 0.5 to 1 percent manganese, between 0.7 and 3 percent silicon, and between 0.1 and 0.3 percent sulfur. This impure mixture is called cast iron or pig iron and is very hard and brittle. It can neither be drawn out into a wire nor pounded into shape. However, its compressive strength is high. Since it is impure, its melting point is lower than that of pure iron, and it can easily be cast into molds. Approximately three-fourths of the pig iron produced is converted to steel. The remainder is poured into molds to give bars of the metal, called pigs, weighing about 150 pounds each.

The blast furnace is built of steel and is lined with fire brick.

When once started, a furnace may be kept in operation until repairs to the lining become necessary which, in some cases, may be after several years. An average furnace may produce 1000 tons of pig iron each day. The annual production of pig iron in the United States varies from 30,000,000 to 45,000,000 tons.

Wrought Iron. One of the earliest forms of iron, used for the shaping of horseshoes, nails, plows, and a hundred other articles useful to our immediate ancestors, was known as forge iron. This was made by heating iron ore and carbon together in small quantities. As the ore was reduced to the metal, a soft mass of iron and slag resulted and by controlling its temperature it could be worked ("puddled"). The product from this process was hammered to remove most of the slag and was heated from time to time in a forge in the smithy which was vital to every town. This produced an iron much purer than pig iron. Consequently it was much softer and could be pounded into shape while hot. The product became known as "wrought" iron. After the blast furnace came into use this older method of making wrought iron could not be applied to pig iron until the carbon was partly removed by heating in the air.

The present day wrought iron is produced in a puddling furnace. In this production the heat of a gas fire is reflected downward from the roof of the furnace upon the charge. This load of material consists of pig iron on top and a layer of iron oxide on the bottom. The iron melts. The oxide oxidizes the impurities which are present. The carbon and sulfur are converted to carbon dioxide and sulfur dioxide and these pass off as gases. Phosphorus and silicon are converted to their oxides, and these are converted again into slag by the addition of limestone. As the impurities in the iron are removed, the melting point of the mass rises. Finally the iron becomes pasty and almost solid. At this point it is raked together and removed from the furnace in large balls. These are rolled to squeeze out the slag. The finished product usually retains about 1 percent of slag which fails to come out. This type of iron is unusually

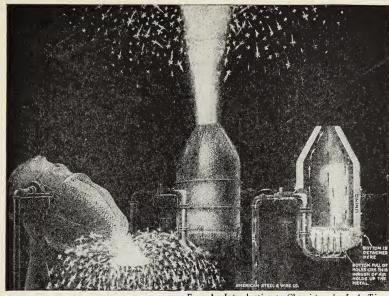
tough and may be shaped. But it does not have the strength of steel. It does not rust as badly as do other forms of iron. The carbon content is usually below 0.1 percent and this accounts for the softness. The presence of the slag gives the product a fibrous structure.

Most of the wrought iron is used to make pipes, tubing, chains, bolts, anchors, plowshares, and horseshoes. Some of this is now being replaced by steels containing very small amounts of carbon. The total quantity of wrought iron produced is about 40,000 tons per year.

Steel. Common usage applies the term steel to a variety of the alloys of iron. As a rule, steel contains between 0.2 and 1 percent carbon in order that it may be sufficiently hard, also it may contain very small amounts of other metals such as manganese, nickel, vanadium, tungsten, chromium, and molybdenum. In general, the methods for the manufacture of steel call for the removal of all impurities by burning and slagging, followed by the addition of the correct amounts of the required constituents. Phosphorus, sulfur, and silicon are especially objectionable in steel because they make it brittle and subject to failure under a load. These, then, must be carefully removed. There are two general methods for the removal of these and other impurities in the manufacture of steel, the Bessemer and the open-hearth processes.

The Bessemer Process. The oldest process for the manufacture of steel is called the Bessemer process after its inventor. This depends upon the fact that the carbon, sulfur, silicon, manganese, and phosphorus which are present in the molten iron will react with oxygen of the air if this is blown through the hot liquid. The Bessemer furnace is called a converter. It is large enough to hold 25 tons of steel and still leave considerable extra room. In the bottom there are more than a hundred holes through which compressed air may be blown. The lining of the converter consists of silica brick held in place with fire clay. It is possible to tilt the converter in order to charge it and to pour out its contents.

Molten pig iron is charged into the converter when it rests



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Fig. 90. The Bessemer Converter

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in a horizontal position. The air is turned on and the converter tipped back to the vertical. The streams of air bring about the violent combustion of the impurities accompanied by colored flames and then a shower of sparks. If you ever fly in a transport plane above Pittsburgh or Gary you will see these flames which are extraordinarily beautiful at night. From the appearance of the flame the operator knows when the impurities have been burned out and the air is then shut off. The time required for this is from 10 to 20 minutes. By the addition of iron alloys to the molten iron, it is possible to form steel having the proper composition. The alloys that are added usually contain manganese and aluminum, or silicon. These elements serve to combine with any oxygen that may be trapped in the molten mass and that would tend to weaken the steel. The converter is again tilted, and the steel is allowed to pour out into large molds where it solidifies in the form of ingots. These ingots which weigh about 2½ tons are placed in hot ovens, called soaking pits, where the strains produced during the cooling gradually disappear. Steel rails, girders, and sheets are produced from these hot ingots by a process of rolling.

The Bessemer converter produces steel rapidly, but this speed makes a lower grade of product. In the short time of twenty minutes, the steel must be made and removed from the converter in order to prevent its "freezing" to the container. There is no time for an analysis of the steel, and, good or bad, it must pass on into the finished product. Another factor against the Bessemer process is the fact that the converter is lined with an acidic material, though a basic lining is used in England. In order to remove phosphorus from the iron it is necessary to add a basic material such as limestone. The Bessemer process does convert the phosphorus to its oxide but the addition of carbon reduces it back to the free element again. The whole answer to this problem is found by using pig iron which contains very little phosphorus, but this means that the iron ore must also contain little of this element. Such ores are obtainable only at higher prices. Another disadvantage is the fact that this process does not permit the use of scrap iron in the manufacture of steel.

Since the Bessemer process came at a time when the railroads were expanding and begging for cheap steel, it is no wonder that it was eagerly welcomed. Such steel as this process produces is satisfactory for rails if all necessary precautions are

observed during the manufacture.

The Open-Hearth Process. A few years after the invention of the Bessemer converter, the open-hearth process was invented. This has undergone a number of improvements until now it produces a good grade of steel and is used to produce most of the steel made. This process depends upon the fact that the impurities in the pig iron may be converted to their oxides upon heating in shallow pans in the presence of an excess of air and iron oxide. The furnace contains a shallow, oval-shaped basin, or open hearth, about 35 to 50 feet long, about 15 feet wide, and about 2 feet deep capable of holding 75 to 100 tons of steel. The lining of this basin is composed of



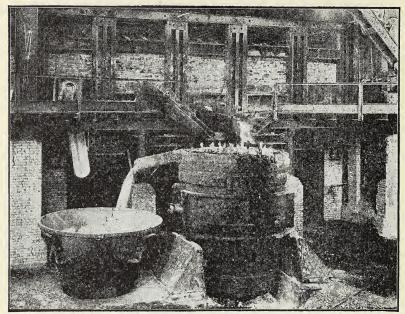
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Fig. 91. Diagram of an Open-Hearth Furnace

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basic material such as calcium and magnesium carbonates. Streams of hot fuel gas and hot air come in at one side and the heat from the combustion is reflected downward by the roof of the furnace. The hot gases from the furnace pass out through a checker-work of brick which becomes quite hot. After a time the air and fuel are permitted to go in over these hot bricks and the combustion products serve to heat up a similar set of bricks on the other side. By shifting the fuel back and forth between these heaters it is possible to save much of the heat which would otherwise be lost and at the same time to elevate the temperature within the furnace.

Chemical Changes Involved. The chemical reactions which occur in the furnace are simple. The first charge consists of limestone which protects the lining of the furnace. This is followed by scrap iron, and then solid, and then molten pig iron. The heat of the furnace melts the scrap iron and decomposes the limestone.



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Fig. 92. Tapping an Open-Hearth Furnace

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At this point a certain amount of iron oxide, in the form of ore, is added, and the quantity of air is increased. The extra oxygen together with the oxide of iron serve as oxidizing agents and convert the impurities to oxides.

While the oxides of carbon and sulfur pass off as gases the other oxides either react with each other or with the calcium oxide (called the flux) to form slag.

$$P_2O_5 + 3CaO \rightarrow Ca_3(PO_4)_2$$

 $SiO_2 + CaO \rightarrow CaSiO_3$
 $MnO + SiO_2 \rightarrow MnSiO_3$

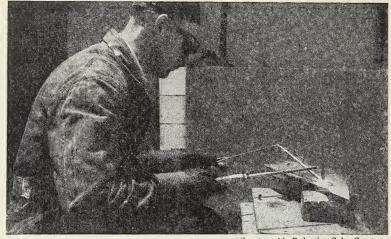
By this process all of the phosphorus is removed from the iron and because of this it is possible to make steel from low-grade ore which is not true of the Bessemer process.

Since the open-hearth process takes place rather slowly it is possible to follow its progress and keep it under accurate control. When a chemical analysis shows that the carbon and impurities are sufficiently removed, the proper amounts of carbon and other elements are added as in the Bessemer process. The furnace is then tapped and the steel poured into ingot molds. The total time for each batch is from 8 to 12 hours.

One great advantage of the open-hearth method is the fact that it permits the use of large amounts of scrap iron and steel and thus empties the huge American junk piles and car lots filled with jollopies that have not another mile in them. Such a use conserves ore, and for many purposes produces a better grade of steel. The charge placed in the open-hearth furnace may contain such scrap material to the extent of more than half of its total weight.

Electric Furnace. Electric furnaces are now being used to produce high-grade steel by further refining the product from the open-hearth or Bessemer furnaces. The steel from such furnaces is of superior quality because of the exact control which the use of electricity permits. The molten metal may be kept for any length of time out of contact with the air and the added metals are given ample opportunity to distribute themselves evenly. Such steel is more dense and finds considerable use in the manufacture of automobile parts and machine tools, the performance of which must be depended upon.

Alloy Steel. Where two or more metals are melted together they tend to dissolve each other and the resulting solutions are called alloys. Because of the automobile, alloy steels have come into very wide use. But now that we have them they are entering many other fields. The constant demand for greater horse-power per pound of engine weight has resulted in the production of high-strength and low-weight alloys for both automobiles and airplanes. Alloy steel which can stand the high temperature and abuse which engine valves must undergo is a



Courtesy Air Reduction Sales Company

Fig. 93. Hard-facing a Plow Share

The alloy steel welded onto this and other equipment increases its life many times over.

wonderful thing. One can easily understand why it has been brought to its present development only after many years of research. The development cannot stop, however, since another alloy is required for the cylinder head, another for the piston, another for the crank shaft, and still others for the frame, springs, wheels, axles, and gears.

The construction of buildings has also drawn upon these alloys. Large amounts of stainless steel are being used to impart both strength and beauty to the exterior of buildings. These contain chromium and nickel. The big field and coast battery guns for national defense must be made from alloys, as must also the foot-thick armor plate which covers fighting ships. Ordinary steel, even though good, cannot withstand the shock of gunfire.

Modern high-speed production calls for machines capable of meeting the demands made by industry. Here the use of alloy steel has increased also. In order to cut steel to shape quickly, it is necessary to have cutting tools that are very hard and that do not lose their hardness even at red heat. The friction of the



Photograph by M. S. MacLean, Jr.

Fig. 94. Arc Welder Joining Steel Pipe

cutting produces so much heat that ordinary tools grow soft and lose their cutting edge very quickly. Alloys containing tungsten make such high-speed cutting possible.

And so the story of alloys may go on and on, the metal worker joining his studies with those of the chemist. The production of the various metals used in the alloys is of major importance to us, and, in general, they are prepared by the processes already mentioned. The actual manipulation will, of course, depend upon the ore available and the method which is most profitable and convenient.

SUMMARY

Metals occur in nature in the form of their oxides, sulfides, chlorides, and carbonates. The less active metals are sometimes found free or native. Those minerals from which a metal may be extracted with profit are called ores.

The process of winning metals from their ores is called

metallurgy. This is done through the steps of concentration, roasting, reduction, and purification. Roasting is for the purpose of converting the ore to an oxide. Reduction is brought about usually by carbon. The active metals are reduced by aluminum or by electricity.

Iron ore is reduced by carbon in the blast furnace. Impurities are converted to slag by the addition of limestone. The product of the blast furnace is known as pig iron or cast iron.

It contains considerable carbon and is quite brittle.

Steel contains known and controlled amounts of impurities. Pig iron is changed to steel in Bessemer converters or in openhearth furnaces. The Bessemer converter burns out most of the impurities within twenty minutes using a blast of air. The open-hearth furnace burns out these and other impurities and converts them to slag. It requires a much longer time and uses iron oxide to supply the oxygen. After the impurities are removed by either method a known amount of carbon together with other metals are added. The Bessemer method is the cheaper but produces a lower grade of steel.

The product from the steel furnace may be further refined in an electric furnace for the production of special alloys and

high-grade tool steel.

REVIEW QUESTIONS

1. Name some metals which occur as native ore. What chemical property determines whether a metal may be found as the free element?

2. List the usual forms in which metals occur as ores. Give examples of each.

3. Outline the principal steps generally required in getting a

metal from its ore.

- 4. What regions supply most of the iron ore in this country? Where is it converted to the metal? Why there?
- 5. What are the important chemical changes which occur in the blast furnace?
- 6. Account for the removal of silicates by the blast furnace process.

- 7. Compare the composition of pig iron with that of steel.
- 8. Describe the chemical changes which occur in the openhearth furnace.
 - 9. Of what importance is the lining of a furnace?
- 10. What are the advantages of an open-hearth furnace over a Bessemer furnace?
 - 11. What are alloys? Why are they of importance?

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FUELS: PRODUCTS OF COMBUSTION

One of the most vital needs for modern living is heat. Everywhere one turns may be seen the smokestacks of industry as well as the chimneys of millions of homes. Enormous wires conduct miraculous electricity from power plants to steel furnaces and electric toasters; thousands upon thousands of railway cars are required to move coal and oil; miles and miles of pipe lines carry natural gas and oil from the production fields to the centers of distribution. The capital involved in the business of supplying fuel has reached such figures that one may compare them with those used in the discussion of astronomy. All of this is true because man needs heat to do things for him. He wants to keep warm, he wants to have light, he wants to make things which require heat, he wants his food cooked, he wants his surgical instruments sterilized, and he wants a machine to do work for him. At the same time we must remember that man must have his own body fuel if he is to do things himself. It is by a process of burning food fuel that man keeps himself warm and gets the energy with which to work.

Let us examine a few common sources of heat. Unless we have a mistaken idea as to their origin we may say that they all derive their fuel value from the sun. Plants which grow utilize an extremely small amount of the sun's energy which falls upon them. Present knowledge indicates that not more than one percent of the energy which comes to the plant is stored there.

Photosynthesis. It was in 1779 that a Dutch physician, Ingen-Housz, discovered the absorption of carbon dioxide by

green leaves placed in sunlight. These green leaves, at the same time, gave off oxygen. Since that time this interesting change, by which man gets his food, his clothing, and most of his shelter, has been the center of intensive research. Within the leaf cells there are small egg-shaped granules called chloroplasts within which the absorption of carbon dioxide takes place. These chloroplasts contain a mixture of a green material chlorophyll, certain pigments, starch, oil, and gelatinous substances. When the light falls on these they absorb carbon dioxide and give off oxygen. We commonly refer to chlorophyll as the necessary catalyst for photosynthesis, but the pigments present in the chloroplasts are also important. These are called xanthophyll (a yellow pigment) and carotene (an orange-red pigment). They always occur with chlorophyll and present information indicates that they perform important functions in the photosynthetic process.

Our knowledge of photosynthesis permits us to write a

chemical equation of a sort.

$$CO_2 + H_2O + solar energy \rightarrow sugars + starch + O_2$$

One worker, by the name of Baly, was able to cause carbon dioxide to react with water when illuminated with ultraviolet light.

$$CO_2 + H_2O \rightarrow O_2 + CH_2O$$
 (formaldehyde)

When the solution was made alkaline the final product was a syrup containing plant sugar. We may write this in the form of an equation.

$$6CH_2O \rightarrow C_6H_{12}O_6$$
 (glucose)

The trouble with this evidence is that plants do not have to get ultraviolet light in order to grow and produce sugars. The reaction which takes place in a test tube may or may not be the one which takes place in a plant leaf.

If glucose is formed within the leaf it is possible for it to be

converted to starch and cellulose $(C_6H_{10}O_5)_x$.

$$XC_6H_{12}O_6 \rightarrow (C_6H_{10}O_5)_x + XH_2O$$

The chloroplasts do contain grains of starch. A large number of glucose molecules take part in the formation of each starch or cellulose molecule. For each glucose molecule which joins in this reaction there is one molecule of water lost. The substance formed is sometimes starch, which the plant stores as reserve plant food, and is sometimes cellulose, which gives the body and rigidity to the plant.

All plants produce more or less oil and proteins. Many times the immature seeds contain large amounts of starch-like material and as the ripening process proceeds the starch content diminishes while the oil content increases. Because of this we are inclined to say that the starch material is converted to oil. How this is brought about we do not know. Similarly we cannot account for the formation of plant proteins. We can, however, take the easy way out and say that they are the products of photosynthetic processes. Such a statement may cover up our extreme ignorance. But we must not be too severe in our criticism. There is much information at hand and many able men and women are adding still more. Possibly we may someday learn the secret; it is not too much to expect.

We can begin to see that our fuels are produced by relatively obscure processes which depend upon light, heat, carbon dioxide, water, and soil fertility. The process of photosynthesis can proceed smoothly only if certain elements are present in the soil. The chlorophyll molecule requires iron for its formation yet iron does not appear in the finished substance. It does, however, contain magnesium. It is extremely interesting to note that the molecule of chlorophyll (C₅₅H₇₂O₅N₄Mg), which is extremely complex, is chemically much like the molecule of haematin which helps to make up the haemoglobin of the blood. They differ in that while the chlorophyll molecule contains magnesium, the haematin molecule contains iron.

Plant Products as Fuels. After the plant is grown it is possible to cut it down, dry it and burn it as wood, or man and other animals can eat it and thereby obtain the energy which originally came from the sun and was stored up in the plant. The material of which the plant is made was mainly carbon

dioxide and water before it became plant tissue. It returns to carbon dioxide and water when man gets through with it. When sugar is converted to carbon dioxide and water it liberates considerable heat.

 $C_{12}H_{22}O_{11}$ (cane sugar) $+12O_2 \rightarrow 12CO_2 +11H_2O +1,349,600$ calories

This heat, you must realize, was absorbed from the sun during the formation of the sugar.

The plant may mature and die without being eaten. In such a case it may lie on the ground to decay. If this happens it is slowly converted to carbon dioxide and water. The heat evolved radiates into the air and to the surroundings. This slow radiation of heat is neither easily nor usually noticed. But we may easily get evidence of such heat production by putting a large amount of decaying vegetable matter in one place. The slow oxidation which occurs produces much heat and in many instances results in a fire. Stacks of newspapers, piles of hay, and bundles of oily rags have been known to catch fire spontaneously. This burning serves to release the heat which originally came from the sun.

The plant may fall in water after it grows and there be covered by other plants. The presence of water stops ordinary decay. Such a submersion and piling up of plants may go on in the same place for many centuries. The compressed material which results is called peat. It still contains most of the original heat energy of the plants. The layer of peat may become covered with dirt by wind or mud from floods so that pressure results. This produces a form of coal. The type of coal formed depends upon the length of time the layer remains. The layer may be subjected to great pressure from the overburden of earth and stone. Heat may result. The bituminous or soft coals have been under tremendous pressure with little heat while the anthracite or hard coals have been subjected to both heat and pressure. The heat drives off most of the volatile matter. Regardless of the type of coal, its burning releases the heat of the sun which has been stored up for so long.

The commonly accepted theory of the formation of petro-

leum and natural gas assumes that these materials have been produced from decaying plants and animals of marine origin buried under soil and rock in huge earthen tight containers. Even though the accumulation of these in certain localities has taken centuries, there can be no doubt that their heat value was derived from the sun.

The energy of the sun causes other changes also. Water which is present upon the surface of the earth absorbs the energy of sunlight and is converted to the vapor form. This change from liquid water to water vapor requires a very definite amount of energy (Chapter 9). The vapor rises in the air. When cooled under the proper conditions it returns to the earth as rain. If the point at which the fallen rain gathers is at a high altitude men can make the plunging water run through a turbine and thereby generate electricity. From the electric current generated it is possible to obtain heat, mechanical work, and chemical energy. This represents a short cycle utilization of the heat of the sun.

The Farm as a Fuel Producer. In the eyes of many experts it seems wise to develop a satisfactory method for the production of fuel on the farm. The wood lot has its importance but the value of the timber for lumber is too great to warrant its general use for fuel. The time factor, too, is against farming for fuel in this manner. In days of very low prices the farmers of the Middle West have been known to burn corn in order to heat their houses. Corn produces a hot fire and is a satisfactory fuel. However, corn is usually worth more as a food than as a fuel. This is a very quick way of getting back some of the heat of the sun and if prices justify such use of corn the farmer is wise to grow his own fuel. It would certainly be a help to farm economy if there were a crop which could be used entirely as a fuel. Such a crop would sell for cash and would balance the farmer's plan of diversification.

Alcohol for Motor Fuel. It is possible to convert the starch contained in corn to grain alcohol by a process which includes fermentation. Within the past few years there has been much agitation for the use of grain alcohol mixed with gasoline as a

motor fuel. As ordinarily produced the alcohol has water in it (95 percent alcohol and 5 percent water) and it will not mix with gasoline unless other substances, called blending agents, are also present. If all the water is removed from the alcohol by special methods, then the dry alcohol and gasoline will mix. In actual use it will be impossible to prevent the entrance of a little water even by absorption on damp days, and since gasoline engines sputter and die if there is water in the fuel, the blending agent must be added in any event. There is no question about the feasibility of using alcohol as a motor fuel. It has been done. But at the present time such motor fuel cannot be produced at a cost which can compete with gasoline. The alcohol may be produced under the most favorable conditions of low prices at about 40 cents per gallon. A gallon of gasoline while burning will liberate about one third more heat than will a gallon of alcohol. You may see that the alcohol price is too great to compete with gasoline on a cost basis. If a better method of production can be found such use may be expected. The Department of Agriculture is investigating the problem.

If all motor fuel had to contain 10 percent of alcohol it would require a very great increase in the annual production of farm crops. Without a doubt this would increase the price of crops and thus further increase the cost of the alcohol, to say nothing of the increased cost of food and feed stuff. If the supply of gasoline begins to run low, however, or cheaper processes are discovered, the use of alcohol for motor fuel in

this country will become a reality.

The Heat Value of Fuels. The principal fuels which man finds ready for his use are wood, coal, petroleum, and natural gas. These may be burned as they appear in nature or they may be transformed into some more easily used product before being burned for their energy. Let us go back to the reaction of carbon with oxygen.

$$C + O_2 \rightarrow CO_2 + 95,000$$
 calories

From this equation we may calculate the maximum heat which can be obtained from a given weight of pure carbon. If the carbon is combined with some other element the amount of heat evolved will be different for a given amount of carbon. When natural gas burns we are dealing with a substance which contains compounds of carbon and hydrogen. The principal substance present is methane (CH₄).

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 210,000$$
 calories

Here we find that the hydrogen of the original compound has been converted into water and thereby contributes some of the heat which we may get by burning the methane. By burning four atomic weights of hydrogen we may get 136,800 calories.

$$2H_2 + O_2 \rightarrow 2H_2O + 136,800$$
 calories

Thus if we burn one atomic weight of carbon and four atomic weights of hydrogen we would expect to get 231,800 calories (95,000 + 136,800). The difference between 231,800 and 210,000 represents the number of calories released when methane is formed from carbon and hydrogen.

In a similar manner we may consider the combustion of the gas acetylene which is used much for the cutting and welding of metals.

$$2C_2H_2$$
 (acetylene) + $5O_2 \rightarrow 4CO_2 + 2H_2O + 624,000$ calories

One molecule of acetylene will thus produce 312,000 calories of heat. If we burn two atomic weights of carbon and two atomic weights of hydrogen we would expect to receive 258,400 calories. We see by this that the molecule of acetylene contains more energy than do the two elements of which it is made. Hence we may say that the formation of acetylene from carbon and hydrogen absorbs 53,600 calories. This extra heat contained in acetylene helps to account for the high temperature which may be obtained with the oxy-acetylene blow torch.

Some fuels such as wood, and most coal, contain combined oxygen in varying amounts. As wood and other plant material is converted into coal it gradually loses water and the oxygen content is lowered. One cannot be sure, of course, of all

the changes which take place but analyses show less and less oxygen and more and more carbon as we go from wood to peat, to lignite, to soft coal, to anthracite. This change also causes the loss of other substances from the material. Even ordinary coal has a higher heat value per pound than does the best of dried wood fuel. The amount of oxygen already combined with the material decreases the heat evolution. As a rule there is considerable water even in well-dried wood and this is vaporized in the process of burning. Such vaporization, as you know, requires 540 calories per gram and thus cuts down the heat evolution still more. Wood, then, is not a very satisfactory fuel from the standpoint of heat evolved.

These considerations of natural gas and wood represent the two extremes of fuels. The others we may classify somewhere in between as regards their ability to evolve heat. Any substance which will combine with oxygen, and in so doing evolve heat, may be used as a fuel. The heat liberated is exactly the same as was absorbed from the sun when the material was

formed from carbon dioxide and water.

Conversion of Fuel to Heat. The proper burning of fuels involves many principles to which chemistry may contribute much. The factors which we have already mentioned from time to time as affecting the speed of chemical reactions are still applicable to this process of burning. Naturally it is the heat which we desire to get from fuels. It is partially the job of the chemist to help find ways for this which are efficient and economical. The modern steam plant does not by any means utilize all of the heat from the coal which is present as it lies in the mine. If we start with a ton of coal in the mine we find that five to six hundred pounds of it is either lost or used up in the process of mining; one hundred pounds of it is used in order to transport the coal to the user; about thirteen hundred pounds of it is burned without useful utilization in the power plant; and that leaves a maximum of one hundred pounds which is converted to useful power. In the light of such figures one feels justified in saying that we are mighty wasteful of the energy which has been stored through the ages, and that the chemists of the future still have a long and useful job to do.

The higher the temperature which can be maintained in a fuel burner the more efficient will be the burning of the fuel. If the fuel is a solid, the rate of reaction is restricted by the surface which is exposed to oxygen. If the solid is powdered the total surface is tremendous. This is utilized in certain mechanical stokers which feed powdered coal to furnaces. Under ordinary conditions the use of fine coal is not recommended because it packs so tightly. However, if the coal is powdered and blown through a nozzle with plenty of air the flame which results is quite hot and may be compared with that produced from burning a gas.

Dust Explosions. The importance of the amount of surface exposed by a combustible substance is noted in the fire hazard which exists in certain industries such as flour mills and coal mines. Flour, starch, coal, wood, and cork are quite combustible and if they are powdered into dust and suspended in the air they need only a spark of some kind to start them burning. Such fine division of the material permits them to burn almost instantly and an explosion results. Such explosions which are destructive of men and materials are far too common. They are known as dust explosions. Modernized flour mills have installed dust collectors at every point in the process where any dust may occur and thus they keep the air free of this menace to safety.

Liquids and Gases Burn Better. It is quite easy to spray liquid fuels into the air in such a way that they burn rapidly. The small particles of liquid offer a great surface to the oxygen in much the same way as the dust particles do. Since most liquid fuels are easily vaporized the small droplets are rapidly changed to gas. When a gas is burned it is probable that the molecules of gas are in direct contact with molecules of oxygen. This brings about rapid and complete combustion. Hence it is desirable to burn liquids or gases where it is possible. In the next chapter we will learn about some of the methods which are used for the production of efficient fuels from coal and petroleum.

The Products of Combustion. In the previous discussion it has been assumed that the burning of fuels results in the formation of nothing but carbon dioxide and water but this is not always the case unless the burning takes place in the presence of an excess of oxygen. While it is true that water always results from the burning of hydrogen compounds, carbon is frequently burned only to the monoxide. Its poisonous nature causes it to be a constant threat to human life. Many people die from it every year. Carbon monoxide is formed whenever carbon or its compounds are burned in the presence of insufficient oxygen. In a coal fire with a deep bed of coal the carbon is first converted to carbon dioxide by the incoming air. The coal in the upper layers is heated by the heat evolved. The supply of air which reaches the fire is not great enough to burn all of the coal which is really hot enough to burn. The hot carbon begins to take oxygen from some of the carbon dioxide.

$$CO_2 + C \rightarrow 2CO$$
 (carbon monoxide)

The gases from the fire will as a result contain some carbon monoxide. This will unite with oxygen if given a chance.

$$2CO + O_2 \rightarrow 2CO_2$$

If the gas is hot and more air is admitted at the top of the fire a blue flame may be seen. This results from the burning of the carbon monoxide. A fire which has been "banked" for the night gives off a considerable amount of this gas. A defective furnace may become a source of poisoning which can spread through the house.

Carbon Monoxide Poisoning. In small amounts, the carbon monoxide present in the air we breathe causes us gradually to suffocate or smother for want of oxygen. In the normal process of respiration the haemoglobin of the blood reacts with oxygen in the lungs. The blood then carries this combined oxygen to all parts of the body where it is given up to burn chemical fuels which are present. Now carbon monoxide has a greater affinity for this haemoglobin than does oxygen. Hence, even small amounts of carbon monoxide which are

breathed into the lungs may step up and grab most of this oxygen carrier. This is made serious by the fact that carbon monoxide is not given up by the haemoglobin as is oxygen. The haemoglobin is thus increasingly tied up until the person affected dies of suffocation. There are other effects such as paralysis of the legs and dulling of the brain which are produced at the same time.

The most common producer of carbon monoxide is the automobile. The mixture of gasoline (a compound of carbon and hydrogen) and air which enters the cylinder is not rich enough in oxygen to burn the gasoline all of the way to carbon dioxide. Thus the monoxide is formed to some extent. Such a large amount of this gas is given off that running an automobile in a closed or partially closed garage for only a short time will snuff out the life of anyone present. The average automobile engine exhausts from one to three cubic feet of carbon monoxide each minute while running idle. A concentration of 0.2 percent breathed for a period of three minutes is dangerous to life. The average garage would become dangerously filled with carbon monoxide after running the engine for only one minute. After five minutes it would be fatal to enter the room.

Carbon monoxide has neither odor nor color and gives no warning of its presence. When it begins to affect a person his mind ceases to function properly and partial paralysis may set in, so that escape becomes impossible even though the danger is vaguely recognized. Very small amounts breathed over a long period of time tend to pile up and produce severe head pains. This is noticed by traffic officers on the corners of busy streets. To prevent danger to drivers it is necessary to ventilate traffic tunnels which go under rivers and buildings. Men who take care of furnaces frequently complain. Open gas fires at home are guilty of producing many cases of illness.

Carbon Monoxide Is Important. Carbon monoxide is not entirely bad. It has many industrial applications. You may recall its use with hydrogen in the production of synthetic wood alcohol as described in Chapter 8. This oxide of carbon combines with chlorine to form *phosgene* (COCl₂) which is

used in the manufacture of drugs and is one of the important war gases. The method for purifying nickel calls for its union with carbon monoxide to form *nickel carbonyl* (Ni(CO)₄). This compound forms at about 50° and boils off from the impurities. It is decomposed to give back the nickel at higher temperatures.

Carbon monoxide is an important fuel. It is formed along with hydrogen when steam is passed over hot coke. The reduction of iron, zinc, and copper oxides is brought about by the carbon monoxide which is present in the furnace. In the blast furnace the principal reaction is between ferric oxide and carbon monoxide.

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

The gas from the blast furnace contains much unused carbon monoxide and this mixture is used as a fuel to run the machinery of the plant. All fuel gas which is manufactured for city use contains this oxide of carbon in amounts up to 35 percent.

Carbon Dioxide. Some of the uses of carbon dioxide have been discussed in Chapter 5. All compounds of carbon, as well as carbon itself, when burned in an excess of air form carbon dioxide. It is produced when limestone is heated as described in Chapter 10. Also, it is formed during the process of fermentation. Animals exhale it when they breathe. The gases from some gas wells contain large amounts of carbon dioxide and the waters from many springs are saturated with it. Temporary hardness of water is due to an excess of carbon dioxide in the form of bicarbonates of calcium and magnesium (Chapter 8). Boiling such water removes the excess of carbon dioxide and permits the carbonates of these metals to precipitate.

Let us look at some of the reactions of carbon dioxide. With water it forms carbonic acid.

$$H_2O + CO_2 \leftrightharpoons H_2CO_3$$

The weakness of this acid together with its harmless nature is shown by its lack of effect upon the delicate tissues of the 312

mouth and throat when it is consumed as soda water. With the salts of metallic elements this acid acts to form carbonates. With calcium salts it forms insoluble calcium carbonate.

$$CaCl_2 + H_2CO_3 \leftrightharpoons CaCO_3 + 2HCl$$

When calcium carbonate is treated with an excess of carbonic acid it dissolves as calcium bicarbonate.

$$CaCO_3 + H_2CO_3 \Leftrightarrow Ca(HCO_3)_2$$
 (calcium bicarbonate)

It is this action which brings about the solution of limestone by underground water forming caves. Water containing this bicarbonate is said to be temporarily hard.

The carbonates are all decomposed by acids. Even the acid of vinegar (acetic acid) causes the evolution of carbon dioxide from sodium carbonate or limestone. With hydrochloric acid the decomposition of limestone is rapid.

$$CaCO_3 + 2HCl \Leftrightarrow CaCl_2 + H_2O + CO_2$$

Carbon dioxide represents the highest stage of oxidation of carbon. By this we mean that no further burning is possible and it will unite with no more oxygen. This suggests its use in fire extinguishers. A fire can burn only so long as oxygen can get to it. If we can put a layer of carbon dioxide between the oxygen and the fire, and keep it there until the combustible material cools, the fire will die. Carbon dioxide is one and one-half times as heavy as air and this alone sometimes makes possible its use to cover a fire. Ordinarily, however, it is better to bring about the evolution of the carbon dioxide at the base of the fire itself. For this purpose the usual fire extinguisher contains two solutions. One is a solution of sodium bicarbonate and the other is sulfuric acid. When the extinguisher is turned upside down the two solutions come together.

$$2NaHCO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O + 2CO_2$$

The pressure of the carbon dioxide forces the liquid out through a nozzle. Most of the gas is dissolved in the liquid and thus is carried to the seat of the fire by the stream. There it is evolved and helps to smother the flame. Another type of fire extinguisher throws a stream of foam and is known as "Foamite" or "Firefoam." This type, too, uses sodium bicarbonate as a source of carbon dioxide. In place of sulfuric acid it uses a solution of alum or aluminum sulfate. You may recall that a solution of aluminum sulfate reacts with baking soda to liberate carbon dioxide (Chapter 10).

$$Al_2(SO_4)_3 + 6HOH \rightarrow 2Al(OH)_3 + 3H_2SO_4$$

The aluminum hydroxide is a gelatinous material which causes a foam with the carbon dioxide. This gas is liberated by the action of the sulfuric acid formed on the sodium bicarbonate. The foam is stabilized or made to stay that way by the presence of an extract of licorice which is placed in with the soda. This type of extinguisher is especially valuable for use on oil fires.

The Cycle of Carbon in Nature. We have seen how carbon dioxide is given to the air by processes of combustion and how it is taken from the air by the process of photosynthesis. The atmosphere is a vast store house for this important gas. Within the ocean water there are countless numbers of minute organisms which absorb carbon dioxide from the water and use it to form their tiny skeletons of calcium carbonate. Some organisms which so use this gas are not so small, the oyster and the clam, for instance. Many tons of this oxide of carbon are thus tied up as calcium carbonate and it is from these bodies that limestone is made. A casual examination of limestone will demonstrate this. This process removes the carbon dioxide from the air more or less permanently though men regain a part of it by heating limestone for lime.

SUMMARY

All growing plants get their carbon for growth from the carbon dioxide of the air by the process of photosynthesis. Chlorophyll is the essential catalyst for this change though light is equally important.

When plants or plant products are used as fuels, the heat

evolved is that which was absorbed from the sun when they were produced from carbon dioxide and water.

The use of coal and petroleum as fuels represents a long time cycle of this use of the energy of the sun. It is desirable to find a short time cycle for this by using farm crops as fuel. The production of acohol may someday meet this need and at the same time use up surplus corn.

The heat value of fuels depends upon the chemical composition of the fuel. The heat which is actually obtained depends

upon the method and completeness of combustion.

Carbon monoxide results from the incomplete combustion of carbon and its compounds. It is a treacherous poison which may be present without our knowing it. It is produced in large amounts from automobiles. Death results from oxygen starvation due to the union of carbon monoxide with the haemoglobin of the blood.

Carbon monoxide is an important fuel and chemical reagent.

Metals are obtained from their oxides by its use.

Carbon dioxide and the carbonates are important industrially. Their uses are many. The atmosphere serves as a reservoir of carbon dioxide for the cycle of carbon in nature.

REVIEW QUESTIONS

1. What chemical change is thought to be the first in photosynthesis?

2. Why should we not compare experiments run in test tubes

with processes which take place in a leaf?

3. Why are we justified in saying that the energy from burn-

ing plants is energy from the sun?

- 4. Calculate the heat which we should expect from burning the carbon and hydrogen contained in cane sugar. Compare this with the amount of heat liberated.
 - 5. Is it true that decaying plants give off no heat? Cite proof.
- 6. What appears to be the difference between various kinds of
- 7. What factors prevent the use of alcohol in competition with gasoline?

- 8. Why do we state that acetylene contains more heat energy than do the elements from which it is made?
- 9. How may we increase the rate and completeness of combustion of solid fuels?
 - 10. Why are gases and liquids the more efficient fuels?
- 11. Account for dust explosions. May they be the result of spontaneous fire?
 - 12. Account for the formation of carbon monoxide in a stove.
- 13. Why do we consider carbon monoxide a treacherous poison?
- 14. The Bureau of Mines states that one volume of carbon monoxide in 2500 volumes of air is dangerous to breathe. How long would be required for an average automobile engine to give this concentration in a room 10 by 10 by 30 feet?
 - 15. Account for the poisonous effect of carbon monoxide.
 - 16. List and describe some important uses of carbon monoxide.
- 17. Why will a solution of sodium carbonate dissolve more carbon dioxide than will a like amount of water?
- 18. Account for the solubility of limestone in underground water.
 - 19. Account for the use of baking powder in bread making.
- 20. Describe the common fire extinguisher. Write the equations for the chemical changes involved during its use.

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FUELS: THEIR UTILIZATION

The United States was born blessed with many things, not the least of which are its abundant supplies of petroleum and coal. The average human being is guided by peculiar instincts in some instances and as a result he becomes wasteful when in the presence of an abundance. His utilization of these fuel supplies has been no exception. Coal has been looked upon as a fuel from an ever full bin. Petroleum products have been a little more difficult to get and thereby probably have enjoyed a greater degree of conservation. We have long since learned that these fuels as found in nature are not always in the form for most efficient heat production. A part of this is true because of mechanical difficulties encountered in their use. Much of it has been learned because of an examination of economic costs.

COAL

Coal has served as our greatest source of fuel. It seems probable that it will still be with us long after our petroleum supplies are gone. It has already been pointed out that we do not utilize much of the substance which lies in the mine as coal. We cannot charge this lack of utilization entirely to waste since a part is used in mining with its operations and a part is used in transportation. We regret to admit, however, that some of our best equipped power plants are able to obtain not more than 30 to 35 percent of the heat value which is in the coal they consume. This fact is an admission of great waste. When we consider that coal is far more than a fuel, that it is a great chemical storehouse, we are faced with the charge of dissipating one of our greatest natural resources.

Coke. For hundreds of years men have used coal in order to obtain iron from its ores. Coal itself was found unsuited for this purpose because it contains too much volatile matter. This was taken care of by first heating the coal to drive off these obnoxious substances. And obnoxious they were indeed. At one time it became necessary for the English government to forbid such treatment of coal near certain cities. There was no need of going to extra trouble in this heating. They merely piled up a great lot of coal and covered it with earth or brick. Around the lower edges they left holes for air and at the top they left a hole where these gases could escape. The whole thing looked much like the classical beehive. A fire was started at each of the lower openings and when the entire mass of coal became hot they filled these holes with clay. The heat drove off the volatile matter and left a steel-gray material having the porous structure of a loaf of bread. This material was excellent for the reduction of iron ore. It became known as coke. This characteristic method of heating the coal became known as the beebive method.

As early as 1792 a Scotch mechanic, William Murdock, conceived the idea of lighting his home with the gas produced by heating coal. By 1816 it was in common use in London on a commercial basis, and by 1817 it was used in Baltimore, Maryland. The commercial production of this gas employed iron retorts in which soft or bituminous coal was heated to about 800° F. No attempt was made to recover the ammonia or the tar which was obtained at the same time.

In 1845, Hoffmann, a German chemist, discovered benzene in coal tar. In 1856 the first synthetic dye was produced, using a compound produced from benzene. Since that time the compounds obtained directly and indirectly from coal tar have greatly increased in number. They have become the starting materials in the manufacture of dyes, explosives, drugs, perfumes, flavors, and plastics. All of this tar is lost when coke is made in the beehive oven.

By-product Coke. During the first World War it became apparent that Germany had great supplies of coal tar from

which to make toluene for T.N.T. The United States was at that time doing little to conserve this valuable material. Most of our coke was being made in beehive ovens according to the old-fashioned method. The necessity of the times forced our industries to install *by-product ovens* which would collect everything as it escaped from the coal.

The by-product ovens are long, narrow chambers built of fire brick. Each is about fourteen inches wide, twelve feet high, and forty feet long. They are heated with gas to about 1000° C. Since they are so narrow the coal in them is heated rapidly. This produces a better coke. Ordinarily these ovens are arranged side by side with as many as one hundred ovens in a single "battery." Each oven holds about fifteen tons of coal. Twelve to fifteen hours of heating is required for the production of coke from this amount of coal. All of the volatile matter is collected.

As the gases come from the coking ovens they are cooled and sent through special equipment where the last traces of tar and ammonia are removed. Additional treatment recovers the benzene and other similar substances as crude benzene. Everything which cannot be removed passes on as *coal gas*. This is a splendid fuel and is used in many cities. From the average ton of coal which is charged into a byproduct oven there is produced: 1400 pounds of coke; 9.25 gallons of tar; 23.25 pounds of ammonium sulfate; 3 gallons of crude benzene; and 11,000 cubic feet of gas. About one third of the gas is used to fire the coke ovens and the remainder is sold as fuel.

Value of By-products. Something of the value of the products of coal distillation may be obtained from the approximate figures for 1939 in the United States. During that year 61 million tons of coal were converted to coke in by-product ovens. This produced a total of 43 million tons of coke, 665 billion cubic feet of gas, 550 million gallons of tar, 1150 million pounds of ammonium sulfate, 50 million pounds of ammonia, and 165 million gallons of crude benzene. The value of the by-products alone was in excess of \$200,000,000.

You will probably think that in the light of such figures all of the coke needed would be produced in by-product ovens. This is not the case, however. In 1939 there were 2 million tons of coal heated in beehive ovens.

Coal Tar. Coal tar contains a number of substances, some of which are volatile. By careful distillation of the tar it is possible to obtain these in the distillate. The first to boil over is the important liquid, benzene, already mentioned. Following this is toluene which was mentioned as the starting material in the manufacture of T.N.T.; xylene, which is very similar to the two above; phenol, which is carbolic acid; cresol, which is the disinfectant used in stock dips, lysol, and creosote for wood; naphthalene, which is the material for the common mothball as well as an important chemical; and anthracene, which is the starting material for certain dyes, notably "turkey red." There are yet other compounds of lesser importance not mentioned here. It must be pointed out that not a single one of these substances is a dye or a drug in the usual sense of the word.

The remarkable part about all of these products is the readiness with which they lend themselves to change by chemical processes. While some of these changes will be discussed in more detail later it must be pointed out that the chemist makes many otherwise unknown substances from these few. He takes these compounds, combines them with a few others obtained elsewhere, and there results a number of new compounds which we term intermediates. They have no particular application except to make still other substances. Two or more of these intermediates may be caused to unite or to react with other compounds and thus produce yet other new substances. The combination and recombination of these steps bring about the production of thousands of hitherto unknown substances which are useful to us in making life more pleasant, in giving us more durable and more beautiful things, and in controlling or curing our diseases. Some of these have been found to have certain effects upon the animal body. This will be discussed in the chapter dealing with drugs.

FUEL GASES

The burning of gases is much more efficient than the burning of solids. This is partly due to the mechanical ease of placing a gas flame exactly where it is wanted and adjusting it to suit the conditions. Of greater value than this is the fact that gases mix with air and their combustion is more complete.

Natural Gas. Just a few years ago natural gas was considered as being in the way of oil production. More or less gas was present in oil fields and it was permitted to escape whenever possible. Many times a well would not produce oil in large amounts until the gas had been released. The writer recalls a visit to a well from which it was claimed 100 million cubic feet of gas escaped each day. Its roar could be heard miles away. Such wastefulness becomes apparent when we realize that fourteen cubic feet of this gas was equal to a pound of the best coal.

The sale of natural gas as a fuel has now become a large industry. In 1939 its production reached the astronomical figure of 2.2 trillion cubic feet. A greater part of this was sold for almost one-half billion dollars. These figures are meaningless, of course, since neither you nor I have any idea of how much they mean. The most outstanding trend in natural gas consumption is in the field of electrical generating stations. Approximately 10 percent of the total natural gas consumption is so used. Its use for domestic and industrial heating is increasing rapidly. In order to get this gas to the consumers there are now great pipe lines which carry it hundreds of miles across the country. One such line runs from western Texas to Chicago with branches along the way.

One great waste in the natural gas industry has been due to the method of producing carbon black. This substance, sometimes called lampblack, is carbon produced by burning gas with a limited supply of air. The smoky flame so produced is kept in contact with a slowly revolving steel drum which is kept cool. A layer of carbon black is formed on the drum and it is scraped off. This finds use in automobile tires since it makes the rubber tougher, and it makes an excellent black pigment for paint, varnish, and black ink. The heat produced in forming the carbon black is entirely lost. It is possible to produce carbon black by heating the gas under the proper conditions, thus decomposing the molecules to carbon and hydrogen.

Manufactured Gas. Besides the production of coal gas during the formation of coke there are two general methods for the conversion of coal into gas. Either of the two methods is entirely satisfactory for use with coke and hence may be used in connection with the manufacture of coal gas.

1. Producer Gas. We have already considered the chemical reaction which takes place between hot carbon and carbon dioxide. This is the basis for the manufacture of one type of gas from coke or low-grade coal. The fuel is burned in a stream of hot air until a white-hot fire results. The air is then shut off and the carbon dioxide is allowed to react with the hot carbon to form carbon monoxide. The two changes which occur may be written in the form of equations.

$$C + O_2 \rightarrow CO_2 + 94,400$$
 calories $CO_2 + C + 53,400$ calories $\rightarrow 2CO$

The formation of one gram molecular weight of carbon dioxide liberates 94,400 calories while the reduction of carbon dioxide to carbon monoxide consumes 53,400 calories for each molecular weight of the dioxide reduced. It must be remembered that a molecular weight of the monoxide is formed from carbon at the same time.

Suppose that all of the carbon dioxide first formed is later changed to carbon monoxide. For every molecular weight (44 grams) of carbon dioxide originally present there will be 41,000 calories of heat left over. This is the difference between the heat evolved by the first reaction and the heat absorbed by the second reaction (94,400 — 53,400). This means that the

carbon monoxide which is formed will be hot. It would be wasteful to cool this down by storage. Hence we find that whenever gas is produced by this process it is used at once in order to take advantage of this extra heat. If it is so used before cooling it gives an efficiency of 85 to 90 percent, based upon the original carbon in the coke. Such gas always contains nitrogen from the air used. The reaction for the burning process is written:

$$2CO + O_2 + (nitrogen) \rightarrow 2CO_2 + (nitrogen) + 135,400 calories$$

Gas produced in this manner is called *producer gas*. Fortunately it may be manufactured from low-grade coal and even from lignite.

2. Water Gas. In our discussion of methods for hydrogen production it was brought out that hot carbon will react with steam to produce hydrogen and carbon monoxide. This is the most widely used method for the production of gas. Coke or anthracite coal is burned with a forced draft of air until the bed of burning material is white-hot. The carbon dioxide formed is sent through a waste-heat boiler in order to recover the evolved heat. The air supply is shut off and steam is forced through the hot coke for about five minutes. The formation of carbon monoxide and hydrogen proceeds so long as the temperature remains above 1000° C.

$$C + H_2O + 41,850 \text{ calories} \rightarrow CO + H_2$$

This reaction absorbs heat from the fire and hence cools the bed of coke. When the temperature falls too low for further action with steam the air supply is again turned on as before. This process is an intermittent one.

The gas produced in this manner is excellent for heating and cooking. It is called *water gas*. Since it contains carbon monoxide, it is poisonous and must be treated with some substance to give it an unmistakable odor.

Some gas plants now make a mixture of producer gas and water gas by feeding air and steam through a deep bed of hot,

low-grade coal. The air supply is adjusted so as to keep the temperature high enough for the reaction with water. The carbon dioxide formed is reduced to the monoxide as it travels upward through the bed of hot material. The product is called semi-water gas.

LIQUID FUELS

The liquid fuels such as furnace oil may be sprayed or blown into any sort of furnace. Because of this ease of handling they are sometimes preferred. With properly designed burners they give high efficiency of burning. With our present use of the automobile and other internal combustion engines, we in the United States require about 600 million barrels of gasoline annually. In order to supply this demand in those countries having low petroleum supplies efforts are being made to convert coal into liquids.

Petroleum (Rock Oil). The crude petroleum which comes from the ground is made up of many different compounds. With the exception of the impurities these are made up entirely of carbon and hydrogen. They are called hydrocarbons. There are thousands of hydrocarbons and it is probable that most of them occur in petroleum. These differ from one another because of the size of their molecules as well as because of the arrangement of the atoms within their molecules. In general, we may say that the fuel use to which particular hydrocarbons may be put depends upon the number of carbon atoms present in the molecules. This may be understood more readily if we add that their volatility is largely dependent upon the molecular weight of the hydrocarbon. Let us consider a few examples. There is one hydrocarbon which has only one carbon atom present in each molecule. This is methane (CH₄) which makes up the greater part of natural gas. It does not become a liquid unless it is cooled to 161.4° below 0° C. Another hydrocarbon found in natural gas is ethane (C2H6). This gas will liquefy if cooled to 88.3° below 0° C. Yet another component of some natural gas is propane (C₃H₈), which liquefies

at -44.1° C. From the gas which is produced in oil fields they are able to obtain *butane* (C₄H₁₀), boiling at $+0.6^{\circ}$ C., and *pentane* (C₅H₁₂), which boils at 36° C. From this you may see that the greater the number of carbon atoms in the molecule the higher the boiling point will be.

Refining Petroleum. If a supply of crude petroleum is placed in a container and heated to a set temperature, everything which can become a gas at that temperature will boil off. By raising the temperature another group of molecules will be removed and we say that the petroleum is being subjected to fractional distillation. Because of the similarity of the different compounds it is impossible to make sharp separations of them by this method. But it is possible to separate the petroleum into "fractions" or "cuts" which boil between certain fairly well defined temperatures. It is possible for the operator to control the products collected in a particular container by watching the temperature within the still. The larger molecules require such a high temperature for their vaporization that the pressure is usually reduced in order to make them boil at a lower temperature.

Uses of the Fractions. Methane and ethane as well as most of the propane content of petroleum are removed by a fractionation which takes place of itself. These first two make up natural gas. Propane and butane (C₃H₈ and C₄H₁₀) are condensed from natural gas and sold in tanks to be used in special systems. We are fast becoming accustomed to seeing the advertisements of "butane" gas. Those homes not having gas available to them find these tanks of butane gas quite convenient.

That portion of petroleum which boils from 35° C. to 70° C. contains pentane and hexane (C₅H₁₂ and C₆H₁₄) and is sold as a thinner for paint and varnish. Molecules containing from five to twelve carbon atoms (C₅H₁₂, C₆H₁₄, C₇H₁₆, C₈H₁₈, C₉H₂₀, C₁₀H₂₂, C₁₁H₂₄, C₁₂H₂₆) are sold as gasoline since they do not evaporate too rapidly in air but do burn satisfactorily in an automobile engine. Those molecules containing from ten to fifteen carbon atoms make up the mixture commonly

sold as kerosene. The ordinary engine will not run with such high boiling fuel but there are some which have been equipped with special heating and vaporizing devices and do burn kero-sene. Much of the higher boiling fractions which possess suf-ficient fluidity are used for fuel oil in Diesel engines and in oil-burning furnaces. As the temperature of the boiling petro-leum goes up, the fractions from which lubricants are prepared come over. Some of these larger molecules are solids and will separate out if the oil is chilled. These solids are sold as "Vaseline" and "paraffin." Little is known about the composition of paraffin. Some refiners go to great pains to effect its removal from their lubricating oils. Others simply add something to prevent the formation of the solid when the oil is chilled (Paraflow). Regardless of which process is followed, it is at once evident that the ultimate user of the lubricant does not want the oil pump and bearings of his car filled with solid paraffin on every cold morning during the winter.

Always there is a petroleum residue which will not boil. If it remains in the still it is converted into a type of coke. If removed it is sold as road tar. The presence of such material which cannot be distilled causes a process of separation as just described to be a batch process. Twenty years ago it was the only process in general use. Modern stills have been devised which process. vised which permit a continuous distillation process. Crude petroleum enters at one point and the various fractions are withdrawn at the proper places from the condenser. They operate on the principle that the higher boiling substances will condense to liquids sooner than the lower boiling ones if their

vapors are sent through a suitable condenser.

This information may be summarized in a list such as that given below. The boiling points given refer to the pure compounds. You may remember that mixtures of substances do not boil at the temperature of the pure substances. As a result, some of the compound which boils at 98° will vaporize along with the compound which boils at 68°. The grouping of the

products is approximate.

A FEW OF THE KNOWN HYDROCARBONS WITH THEIR BOILING POINTS

Name	Formula	Boiling	Used for
		Point °C.	
Methane	CH_4	-161.4	NT . I
Ethane	C_2H_6	— 88.3 \	—— Natural gas
Propane	C_3H_8	— 44.1	
Butane	C_4H_{10}	0.6	—— Butane gas
Pentane	C_5H_{12}	36.0	
Hexane	C_6H_{14}	68.7	—— Paint thinner
Heptane	C_7H_{16}	98.4	
Octane	C_8H_{18}	125.6	—— Gasoline
Nonane	C_9H_{20}	150.7	Gasonne
Decane	$C_{10}H_{22}$	174.0	
Undecane	$C_{11}H_{24}$	195.8	
Dodecane	$C_{12}H_{26}$	216.2	Kerosene
Tridecane	$C_{13}H_{28}$	234.0	Kerosene
Tetradecane	$C_{14}H_{30}$	252.5	Fuel oil
Pentadecane	$C_{15}H_{32}$	270.5	
Hexadecane	$C_{16}H_{34}$	287.5	Lubricants
			Vaseline
	-		Paraffin

Gasoline Production. The best petroleum rarely contains more than 25 percent of compounds which can be used for gasoline. If this were the only source of motor fuel we would have to produce four times as much crude petroleum as we consume in gasoline. Putting that much crude petroleum through the refining process would call for the production of like amounts of kerosene, fuel oil, lubricating oil, paraffin, and road oil. A great excess of these other products would depress their market value to the extent that gasoline would have to be sold at a much higher price. This information was well known to the early gasoline producers when it looked as if the automobile industry was going to outrun the capacity for the refining industry to produce gasoline. This threat furnished the incentive for research on the production of greater amounts of gasoline from crude petroleum. These efforts have produced results which are entirely satisfactory.

Cracking. In 1869 it was discovered that the distillation of high boiling petroleum fractions under thirty to forty pounds of pressure brought about the production of lower boiling substances which could be used for burning. Since 1913 this general process has been employed for the production of gasoline. The first installation was originated by Burton and bore his name. It was a simple pressure distillation. There have been numerous modifications of this process. As the materials of construction have been improved it has been possible to increase the pressure upon the liquid being distilled. The old tank of boiling liquid has been replaced by complex systems of pipes, like boiler tubes. At the present time pressures of more than 1000 pounds per square inch are employed. Temperatures required for the distillation have increased to over 600° C. Such plants are able to start with fuel oil and convert 70 percent of it into gasoline suitable for the average motor car.

The chemical changes which take place during this heating process are best described as decompositions. Under the conditions it is possible for some of the decomposition products to recombine and thereby form new substances which are suitable for gasoline. Such a process has been termed "cracking." Because it is brought about by heat it has lately been called *thermal cracking*. Such treatment of petroleum has led to the production of large amounts of gas and much cokelike material. The proper utilization of these has been a problem.

Since 1913 there has been a saving of 13 billion barrels of crude oil just because of the extra gasoline produced by cracking. In 1939 alone 1400 million barrels of crude oil were thus conserved. The cracking units which brought about this conservation of our national resources were built at a cost of \$450,000,000. More than half of the gasoline now used has been produced by some process of cracking.

Catalytic Cracking. Within the past few years there have been remarkable developments in the field of gasoline production. Research workers now look upon the cracking of petroleum products as another chemical reaction which is af-

fected by the presence of a catalyst. It has been demonstrated that certain claylike substances catalyze the cracking process and bring about a greater production of gasoline. It may well be that these catalysts speed up the formation of the desired substances from the broken-down fragments of molecules. The gasoline produced is of a much higher grade than that now used in automobiles. It is mixed with gasoline from the thermal cracking process and thus improves the quality of that product. It is claimed that road oil may be converted to high-grade (premium) gasoline with a yield of 80 percent. This method, too, results in the formation of large amounts of gas.

Polymer Gasoline. Within the past few years the gasoline industry has learned how to make the waste gases from the cracking plants into gasoline. In the presence of certain catalysts such as phosphoric acid, sulfuric acid, aluminum chloride, and boron fluoride some of these small gas molecules will combine to form larger ones. Much of the gasoline so made is suitable for airplane use. By the use of refinery and natural gases it is possible to make a total of 300 million bar-

rels of this gasoline annually.

Anti-knock Gasoline. Another means of protecting gasoline reserves is to increase the efficiency of automobile engines. This is usually done by increasing the compression within the cylinder. Under such conditions the gasoline vapors and the air within the cylinder are put under tremendous pressure just prior to their ignition by an electric spark. With ordinary gasoline at higher pressures there is an unpleasant knock or "ping" when the explosion occurs. This results in a great loss of power. To get away from this knock the gasoline producers tried all sorts of things. Some of them mixed benzene, from coal tar, with their product; others mixed the cracked gasoline with that produced by straight distillation. For some unknown reason each of these mixtures produced less knock in an automobile engine than did the straight-run gasoline. One group of investigators experimented with the use of volatile metallic compounds. Out of this work came tetraethyl lead

(Pb(C₂H₅)₄), or ethyl fluid, which is now in general use. Only a very small amount of this substance is added to gasoline in order to eliminate most of the knock. Unfortunately, it is extremely poisonous and offers a considerable hazard to those who make it and to those who blend it with gasoline.

It is not enough to know how to get rid of the knock in an engine. It is much more important to know what causes it. Those interested in these investigations have measured the pressures in the cylinders, before, during, and after the explosion of the fuel. They have changed the design of the combustion chamber. Someone suggested the use of a glass head in the cylinders so that they could see what took place. Through such a head they took high-speed moving pictures of the burning fuel in an engine running with ordinary gaso-line and then with anti-knock gasoline. They began to see the cause for the knock. Ordinary gasoline in a high compression engine burns almost all at once. The introduction of anti-knock material causes it to burn much more slowly. Hence the piston is given a push in place of a sledge-hammer blow. Lead tetraethyl retards the combustion and, as you may expect, it is called a negative catalyst. Its effect on the rate of combustion is partially determined by the composition of the gasoline.

Octane Number. In the search for information about which fuels produce a knock it was discovered that a substance known as *iso-octane* produced almost no knock in any ordinary engine. Another substance, *heptane*, appeared to be the worst. By the use of mixtures of these two substances it was possible to set up a series of standards of anti-knock values. Pure heptane was given a rating of 0, while iso-octane was given a rating of 100. So-called "low test" or "plain" gasoline which knocks like a mixture of 60 parts of iso-octane with 40 parts of heptane in a standard engine is said to have an *octane number* of 60. Regular gasoline has an octane number of 72 to 74 though this varies and is being raised by some manufacturers. The trade-marked "ethyl" gasoline has a rating of 80 to 82. Any fuel which knocks worse than heptane is given a rating

less than zero and any fuel knocking less than iso-octane is

given a rating greater than 100.

Most of the gasoline sold today contains lead tetraethyl. Though it is not branded with the ethyl name it must be handled in equipment which states that it contains lead. The addition of this ethyl fluid to gasoline is equivalent to raising the octane number of the fuel. It becomes a question as to how much ethyl fluid a person can afford to pay for. There is a limit to the response obtained from higher octane gasoline as used in an ordinary engine. Unless the engine has a very high compression it is probably more economical to use the regular grade of gasoline.

The refineries have seen millions of dollars pass from the consumers into the hands of those who prepare ethyl fluid. This, as a rule, represents a premium price which motorists are willing to pay. Any process by which the refiners can raise the octane number of their gasoline will mean premium profits to themselves. You may rest assured that they have not been asleep. The cracking process produces a gasoline with an octane number greater than that of straight-run gasoline. More than one fourth of the gasoline produced by distillation of petroleum is run through a cracking process in order to bring its octane number up. The thermal process of cracking when applied to gasoline will raise the octane rating to about 70. The gasoline from catalytic cracking may have an octane number as high as 90 though 80 is probably the average. Polymer gasoline produced by catalytic union of the small molecules of gases may have an octane number of 90 to 100. If these are mixed with poorer gasoline it will give a satisfactory fuel for automobiles. The refiner must decide whether to bring the octane number of his product to an acceptable value by the use of ethyl fluid or by the use of these higher octane gasolines. At the present time they combine the two except in a few cases.

Aviation Gasoline. In 1928 the average military airplane used gasoline with an octane rating of about 60. In 1931 this was raised to 87. Those planes which were designed for the

new fuel were able to give 33 percent more power per unit of weight. Many planes now in use are able to use 100-octane fuel and they show another 30 percent increase in power over those using 87-octane gasoline. Translated into actual figures it is claimed that a plane using 100-octane fuel is able to take off in 20 percent less distance, and can climb 40 percent faster than one using 87-octane. In the case of a transport plane these facts mean money. The plane using the higher octane fuel on a 1400-mile flight can carry 1200 pounds less gasoline and take on seven more passengers, or their freight or mail equivalent. If we look at war in the light of reality we may see what this means in terms of effectiveness for the bomber. The fighting plane which can maneuver rapidly has an advantage. The use of high quality aviation fuel means a more perfect air defense, the winning of aerial battles, and a greater safety for the fliers.

The United States is far ahead in the production of aviation gasoline. By treating certain of the refinery gases together with certain natural gases with suitable catalysts, blending the products and adding some ethyl fluid, it is possible to produce about 6000 million gallons of 100-octane gasoline annually. It is claimed that the oil industry of this country will be able to supply enough of this high-grade fuel to meet the entire civil and military needs of the world. The refiners fully expect the use of this fuel in automobiles in the not too distant future. In the light of recent trends their claims and expecta-

tions are probably correct.

Petroleum in the Future. Within recent years it has been proposed by experts that petroleum is being formed all of the time. Our present methods of conservation and utilization are helping greatly to maintain our known reserves. It is claimed that we should have ample petroleum to meet all of our needs for thousands of years to come. To sit idle and trust in this seeming everlasting supply would be folly. Other fuel sources are being sought. There are, for example, enormous amounts of oil-bearing shale all over the world. If the price of petroleum gets high enough these deposits will be

dug up and their oil distilled out. We have already mentioned the use of alcohol as a possible substitute in motor cars.

Liquids from Coal. The first practical production of liquid hydrocarbons from coal was accomplished by Bergius in Germany in 1924. He was able to treat coal with some oil and hydrogen and get gasoline-like liquids from it. This process has been improved since then, and there are now plants which produce motor fuel on a large scale, although they may have been blown up by bombs by the time this is in print. In general, the coal is crushed to a powder and made into a paste with heavy oil and a catalyst such as tin or lead. It is pumped with hydrogen at 4000 pounds pressure into a heater where the temperature is raised to 400° to 480° C. for two hours or more. The gaseous products which distill are treated at the same temperature and pressure with additional hydrogen in the presence of more catalyst. The yield of the process is about 170 gallons of motor fuel for each ton of dry coal used. This amount of coal uses up 48,000 cubic feet of hydrogen in its treatment.

That the process is expensive there can be no doubt. It exists by reason of a protective tariff. One plant at Leuna, in Germany, has an output of 250,000 tons of motor fuel annually. At the present time this process is not able to compete on a cost basis with petroleum in the United States.

Comparison of Fuel Values. It will be of interest to compare the fuel values of the various types of fuel which we have discussed. These are listed below. The usual method of listing these is in terms of *British Thermal Units*. This is the amount of heat required to raise one pound of water 1° F. It takes approximately 4 British Thermal Units (B.T.U.) to equal 1000 calories.

Comparative Heat Values of Fuels				
Name of Fuel	B.T.U. per pound			
Wood, dried	8,000			
Coke	12,900			
Coal, anthracite	13,500			
Coal, bituminous	14,400			

Name of Fuel	B.T.U. per pound
Fuel oil	18,500
Kerosene	20,000
Producer gas	156 per cubic foot
Water gas	300 per cubic foot
Coal gas	600 per cubic foot
Natural gas	1,100 per cubic foot

From this you may see that it will pay to consider the price of fuels in terms of their relative heating values. Such consideration is the only sound basis for the expenditure of money for heat.

SUMMARY

Because of inefficiencies the best coal-burning power stations are able to utilize only a third of the heat value of the coal which they consume.

Coke is made by the wasteful beehive method and by the by-product method. The latter was brought into use to conserve the gas, tar, and ammonia obtained during the coking process. Most of the coke is now made in by-product ovens.

Coal tar is a source of valuable chemical compounds. These in turn are useful in the preparation of many other compounds. Coal gas is a useful fuel.

Much of the waste of natural gas is being eliminated by sending it through pipes to cities. Its use in power production is increasing.

Fuel gases may be produced from coal or coke by the producer gas method or by the water gas method. Producer gas should be used as it is made because it is hot. Much manufactured gas is a combination of these two kinds of gas.

Petroleum is composed of hydrocarbons. The use of particular hydrocarbons depends upon their volatility which in turn is partly determined by their molecular weight. Petroleum refining brings about the partial separation of these hydrocarbons into fractions with suitable volatility.

Much gasoline is produced by cracking the high-boiling fractions. This is done by thermal and catalytic methods. Much

crude petroleum is thus conserved. Natural and refinery gases

are now made to combine to produce polymer gasoline.

The knock in an engine is produced by the too rapid burning of the fuel in the cylinder. This may be decreased by mixing benzene, cracked gasoline, polymer gasoline, or lead tetraethyl with the gasoline ordinarily used. The anti-knock value of a gasoline is based upon mixtures of iso-octane and heptane. It is called the octane number.

The production of high anti-knock gasoline is now a question of equipment and engine design. The petroleum industry is able to keep ahead of the demand. Airplanes may use 100-octane fuel with greatly increased power and efficiency.

Germany uses coal as a source of motor fuel. It is produced

by a process of hydrogenation.

REVIEW QUESTIONS

1. Compare the beehive and by-product methods of coke production. What is the advantage of one over the other?

2. List the products obtained from the by-product oven.

- 3. What principal products are obtained from the distillation of coal tar? Give their chief uses.
- 4. Why do the substances obtained from coal tar have such value to the chemist?
- 5. Why do we consider it wasteful to produce much needed carbon black by the incomplete combustion of natural gas?
- 6. What substances make up natural gas? Give their chemical formulas.
- 7. Outline two methods for the production of fuel gas from coke.
- 8. Write the chemical equations for the changes involved in your reply to question 7. On the basis of the equations show which should be the better method.
- 9. Why do we notice such a vile odor when manufactured gas escapes from the kitchen stove?
- 10. By what general process are the various products obtained from petroleum?
- 11. What determines the use to which various petroleum fractions may be put?

- 12. If you know the boiling point range of a petroleum fraction can you make a good guess as to the molecular weights of the molecules in the fraction?
- 13. List the common petroleum products and give the approximate composition of each.
- 14. What appears to be the general method of naming hydrocarbons?
- 15. What difference do you notice in the formulas of the hydrocarbons as you go from the smallest molecules to those larger?
- 16. What methods are used to increase the gasoline yield of petroleum? How are they carried out and what is their economic effect?
- 17. What do we mean by polymer gasoline? Do you see any connection with the true meaning of the word polymer?
 - 18. What is the immediate cause of the knock in an engine?
 - 19. What is ethyl fluid? What sort of catalyst is it?
- 20. What is the basis of octane numbers? Inquire as to the octane rating of the three types of gasoline sold at a nearby service station.
- 21. What do we mean by straight-run gasoline? How may its octane number be improved without the use of ethyl fluid?

 22. What is the advantage of high-octane gasoline for airplanes?

 23. What is the general process for the production of liquids
- from coal?
- 24. It requires two tons of bituminous coal to heat a certain house for a month. The price of coal is \$6 per ton. The price of natural gas is \$0.60 per thousand cubic feet. If the efficiency of burning coal is 30 percent and that of gas is 85 percent calculate the comparative costs of the two fuels. You may substitute the particular figures for your own city.

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THE HYDROCARBONS

In previous discussions we have mentioned a few of the compounds of carbon and hydrogen which are called hydrocarbons. Some of these are found in petroleum, and others are the products of coal distillation. We have implied that these hydrocarbons are extremely important. Actually, though, their real importance is almost beyond comprehension. If we consider them as fuels only, we may say they are worth so much money per ton. However, it is not so easy as this to assign a value. Now that we have them in chemical plants and drug stores, we can buy them or sell them for certain amounts. But there are many things produced from them that could be had only at very high prices, or not at all, if we could not take advantage of research knowledge and new processes in treating the hydrocarbons as chemical compounds. Because of thousands upon thousands of painstaking experiments which have been performed during the past hundred years, this knowledge and these processes have increased to the point where we are just now beginning to realize the tremendous value which these hydrocarbons have. Petroleum refineries are finding themselves being pushed into the manufacture of synthetic organic chemicals from products which were thrown out on the slag heap or poured down the drains as waste only a few years ago. You may recall that the original production of coke from coal resulted in the loss of many valuable byproducts which were either burned or thrown away. A similar thing has been going on in the petroleum refinery.

Compounds of Carbon Are Complex. Thus far our discussions have centered around things such as water, salt, sand, and sulfur which we class together as being *inorganic*. By this we

mean that they are not produced by the processes of organized life. The carbon compounds, on the other hand, were first obtained from things then alive or that had been alive. Because of this they have been called *organic* and the name is still used even though these same compounds may be produced in the chemical laboratory without the use of plants or animals.

Most of the inorganic compounds which we have studied are made up of relatively small molecules. These have been found to take part in a few general types of chemical reactions. Some of these inorganic substances are necessary for the proper growth of plants, animals, and human beings but the live growth itself involves organic compounds. As a rule, the organic compounds are far more complex than are the inorganic compounds, and the chemical reactions which they

may undergo are sometimes extremely complicated.

The chief reason for the complex nature of organic compounds lies in the fact that carbon atoms may unite with atoms of other elements, and, at the same time, they may also unite with other carbon atoms which also have united with atoms of other elements. This permits the formation of large molecules which may contain a considerable number of different elements. Now this could be and could continue to stay very confusing. But scientists have orderly minds. They cannot stand confusion and muddling. Hence in order that the organic chemist may approach his work with intelligence, scientists have classified the information which has been collected over the years. As in all chemistry, the most simple classification of these chemical reactions depends upon the elements which are present in the organic compound.

Hydrocarbons. The simplest organic compounds known are those containing carbon and hydrogen only. These are always called *hydrocarbons*. Because of the ability of carbon atoms to unite with each other and with other elements at the same time, we find that there are many thousands of these hydrocarbons known, listed and classified. Without doubt there are still many others which have never yet been obtained in pure form. Now let us observe how the chemist ap-

proaches the problem of putting his stock of hydrocarbons in order.

We have already mentioned methane (CH₄), ethane (C_2H_6) , propane $(\dot{C_3}H_8)$, and butane (C_4H_{10}) , which occur in natural gas. These are the more simple compounds of carbon and hydrogen. In the preceding chapter we have listed these and other hydrocarbons having molecules which are larger. An inspection of the formulas given will show that the molecules of these substances differ from each other by CH₂ as we go down the list. These formulas have been obtained by chemical analyses as outlined in Chapter 7. All of these substances are classed together in what we call a homologous series. This particular homologous series is known as the methane series. There are other homologous series also and we find that they, too, differ in their formulas by CH2. Since it is impossible to see the individual molecules of hydrocarbons we must depend upon what we shall term their chemical properties in order to list them in these series.

Saturated Hydrocarbons. The hydrocarbons of the methane series do not take part in ordinary chemical reactions. Methane itself will not combine with oxygen unless it is burned. The higher boiling liquids are purified by treatment with concentrated sulfuric acid. We know that ordinary lubricating oil must be very resistant to union with oxygen even when quite hot because it certainly gets hot enough to be destroyed if it did unite with oxygen in the automobile engine. A highly purified hydrocarbon mixture is sold as "Nujol." It is odorless and tasteless and is used as an intestinal lubricant since it passes through the digestive tract unchanged by either body heat or digestive juices. Because of this relative chemical inactivity these hydrocarbons are called "paraffins," a name which indicates that they have "little affinity" for other things.

A possible reason for the inert nature of these hydrocarbons is obtained by a consideration of their formulas. Let us now write out the formula for methane and consider how its molecules may be put together. Since one carbon is united with four hydrogens we may assume that the hydrogen atoms are spaced around the carbon atom.

We like to think of the carbon atom as being a small globe and then we like to think of the hydrogen atoms as being attached to the carbon atom at equal distances from each other. The resulting molecule, of course, occupies three dimensions though we can represent only two of these on a flat sheet of paper.

When we discussed the formation of sodium chloride (Chapter 14) that change was represented as involving a transfer of electrons from an atom of sodium to an atom of chlorine. Sodium chloride has been found to exist as ions.

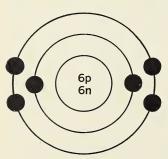


Fig. 95. Structure of Carbon Atom

Methane, however, gives no ions at all, and hence we cannot assume that it was formed in the same way that sodium chloride was formed. Faced by this difficulty, the chemist had to create a new picture that would fit. Let us look at his concept of the carbon atom. From its position in the periodic table (in the center of the top row) we would expect carbon to have four electrons which are available to act as valence electrons

(Chapter 14). The carbon atom may either give up four electrons or take up four electrons to form a stable configuration. If it gives up four electrons it will look like a helium atom and if it takes up four electrons it will look like a neon atom. Since this balance would probably result in equal tendencies to lose and to gain electrons we assume that carbon just shares its elec-

trons when it reacts with other atoms. It may be recalled that we term this *covalence*. The simple molecule of methane (CH₄) may then be written as shown in the figure. Remember that the small circle represents the atom nucleus.

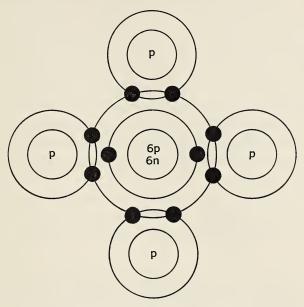


Fig. 96. Structure of Methane Molecule

In this figure the hydrogen atoms furnish one electron each to be shared with the carbon. An electron from the carbon atom is also shared by each hydrogen atom. The two electrons give hydrogen a stable pair like helium and the carbon has its stable eight electrons like neon. We can write this formula more simply if we let the symbol of the element represent all of the atom except the outer electrons. Thus, for carbon

we may write $\cdot \dot{\mathbf{C}} \cdot$ and for hydrogen H. The molecule of

The attractive forces between the atoms within the methane molecule must be great since the molecule sticks tightly together. Because it sticks together so firmly it has but little tendency to react with other things. The combining number (valence) of carbon is four. We can see that if any other element were to combine with methane it would have to displace a hydrogen atom first. Those hydrocarbons which are so chemically satisfied are said to be *saturated*. We must not, however, assume that all hydrocarbons are so fully satisfied and so strongly knit together as methane. We shall, in fact, soon discuss some hydrocarbons which will easily react with chemical reagents and they are said to be *unsaturated*.

Now let us apply these ideas to some other hydrocarbons. We mentioned that ethane (C_2H_6) occurs in natural gas. This may be written as

After we have once written out a formula to show the electrons we may let a short straight line represent a pair of shared electrons as is done on the right. In order for ethane to react with anything else, it would first have to lose a hydrogen atom or the two carbon atoms would have to split apart.

The third member of the series which also occurs in natural gas is called propane (C₃H₈). The formula for this may also be written in two ways.

We may continue to write the formulas of other "paraffin" hydrocarbons in this way. The string of carbon atoms tied together is called a "chain." Sometimes this chain runs to

great length as in one known compound which has 60 links of carbon atoms united.

Isomers. During the progress of hundreds of laboratory experiments chemists work patiently and endlessly to get substances which are as pure as it is humanly possible to make them. To be sure of their purity it is usual for them to make an accurate analysis of the new stuff which is checked against the analysis of the pure compound. Chemists have carried on work of this kind with the hydrocarbons present in petroleum. You can imagine, then, the bewilderment of a laboratory worker when he discovered by his analysis that there were two compounds with the formula C_4H_{10} . These two were both pure substances. They were almost alike in their properties. But their boiling points were definitely different. Further investigation showed that petroleum also contains three substances with the formula C_5H_{12} , and five substances with the formula C_6H_{14} . It is queer things of this sort which whip the life of a chemist into both the keenest interest and occasional despair.

At first it seemed impossible that there could be two or more hydrocarbons with the same formula. A satisfactory explanation was finally found, however, by a careful consideration of how the molecules may be put together (their structure). The ordinary way of writing the structure of C₄H₁₀ (butane) is to put all of the carbon atoms together in a so-called "straight chain."

also written CH₃CH₂CH₂CH₃

It occurred to someone years ago, however, that the carbon and hydrogen atoms may be arranged in a different way. It is possible to write this with a branched chain in which more than two carbon atoms are linked to another carbon atom.

also written CH₃CH(CH₃)CH₃

There is no other arrangement which can be given to this formula. The two formulas given should represent two different substances having the same chemical composition. Since there are actually two different butanes known, it begins to look as if there may be something to this sort of thing.

Now let us apply this same method of shifting atoms around to the pentanes (C₅H₁₂) which have been discovered. One of these may have a straight chain molecule.

also written CH₃CH₂CH₂CH₂CH₃

Another pentane may have four carbon atoms in a row and the fifth branched off.

also written CH₃CH₂CH(CH₃)₂

Still another pentane may have two crossed chains of three carbon atoms each. This molecule is peculiar in that one of the carbon atoms is attached only to other carbon atoms.

also written CH₃C(CH₃)₂CH₃

Since there are only three compounds known with the formula C₅H₁₂ it seems possible that our system may be correct.

This same idea may be applied to the hexanes which have the formula C₆H₁₄. This may be written in just five different arrangements, and there are just five different hexanes known. From all of this we are able to say that the way in which a molecule of a substance is put together has something to do with its properties. As the number of carbon atoms increases, the number of possible arrangements of the atoms within the molecules increases at a tremendous rate. For example, it is calculated that there are more than 100,000 different structures possible for C₂₀H₄₂. A few of these are known, and they occur in the common paraffin which we as children used to chew like gum and which our mothers used to seal glasses and jars of jellies against air, dust, and bacteria.

Compounds which have the same formula, yet are different because of the way in which the molecules are put together, are called isomers.

Unsaturated Hydrocarbons. In the production of gasoline by the cracking of petroleum, there is another type of hydrocarbon produced which seems to be quite different from the saturated ones. The simplest one of these has the formula C_2H_4 . No one has ever been able to isolate a hydrocarbon with the formula CH_2 . The substance C_2H_4 is a gas known as ethylene. It is finding a wide use in medicine as an anesthetic in place of ether. Ethylene is being employed, too, by fruit

growers and shippers because it causes fruits such as oranges and bananas to take on an even yellow color. These fruits, shipped green, are usually transported in freight cars or stored in rooms containing ethylene so that they will present a better appearance for sale. This practice is not at all objectionable since these fruits ripen before their skins turn yellow. At such a stage they are still firm enough to resist damage due to handling. If kept until they naturally turn uniformly yellow quite a loss due to overripe fruit will be taken by the dealers. If the family can buy these fruits in their early stage of ripening it means less losses for them also because of greater keeping qualities.

Ethylene is very reactive chemically. It combines rapidly with sulfuric acid, hydrochloric acid, or chlorine. In the presence of a catalyst such as powdered nickel, ethylene will re-

act with hydrogen to form ethane.

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

Because of this chemically unsatisfied nature of ethylene it is said to be *unsaturated*. It seems as if part of the valences of the carbon atoms have not been used in holding the molecule to-

gether.

We tried to account for the chemical inactivity of the saturated hydrocarbons by considering the structure of their molecules. Now let us try to explain to our satisfaction the great chemical activity of ethylene by the same method. In ethylene molecules there are two carbon atoms and four hydrogen atoms which must be arranged together. Each carbon atom has four external or valence electrons, and each hydrogen atom has one. If we try to write the electronic structure we get something like this:

Each carbon atom has an extra electron which is not shared with another atom, and, at the same time, each carbon atom needs an additional electron to make up the required eight electrons. Suppose we let each carbon atom help the other out by sharing these extra electrons. We then may write the structure as:

This may also be written as:

We may now explain the great reactivity of ethylene by assuming that it may exist in either of the two forms.

The form represented by the formula on the right presents a single electron on each carbon atom which may be shared by other atoms. The reaction of ethylene with hydrogen may be shown as follows:

$$\begin{array}{c} H \ H \\ H \colon \overset{\cdot}{C} \colon \overset{\cdot}{C} \colon H + H \colon H \to H \colon \overset{\cdot}{C} \colon \overset{\cdot}{C} \colon H \\ \vdots \\ H \ H \end{array}$$

In such a reaction we find that the reagent, or whatever reacts with the ethylene, always adds to the ethylene molecule. It is not necessary to displace a hydrogen atom or to break apart the carbon atoms.

Ethylene Series. Now there are many other compounds which exhibit the same kind of reactivity as does ethylene. Ethylene itself has two hydrogen atoms less per molecule than does ethane (C₂H₆). There is a whole series of compounds which lack two hydrogen atoms per molecule of being saturated. A few of these are listed.

The structural formulas given above are for the straight chain molecules only but these are by no means the only ones known. All of the molecules with four or more carbon atoms may exist as isomers. For example, the carbon chain may be branched and also the "double bond" (C = C) may be between other than the two carbon atoms at the end.

All these hydrocarbons may be changed to saturated hydrocarbons by the addition of two hydrogen atoms to each molecule. In this respect they are like ethylene and are classed together as the *ethylene series*. The formulas differ within the series by CH₂, and thus this series is also said to be *homologous*.

Polymer Gasoline. One of the most useful reactions of unsaturated hydrocarbons is their ability to combine with other unsaturated hydrocarbons. In some cases they will combine with certain saturated hydrocarbons as well. This type of reaction is illustrated in the formation of polymer gasoline. For instance, one type of installation utilizes isobutane together with isobutene in the presence of a catalyst such as sulfuric acid or phosphoric acid.

$$\begin{array}{c|ccccc} CH_3 & CH_3 & CH_3 & CH_3 & CH_3 \\ & & & & & & & & & \\ CH_3-C-H + CH_2 = C-CH_3 \rightarrow CH_3-C-C-C-C-CH_3 \\ & & & & & & & \\ CH_3 & & & & & & \\ iso-butane & iso-butene & iso-octane \\ \end{array}$$

The gases used are those which come from natural gas and cracking gas and in spite of purification they are never pure. Other substances are formed at the same time but the mixture has a high octane number.

Another such reaction of considerable interest has been announced within the past few months. Iso-butane is made to react with ethylene. The temperature is near 775° C. and the pressure is between 25 and 50 pounds per square inch. No catalyst is required. The product has an exceptionally high octane value and with other high octane fuels and ethyl fluid will yield an aviation fuel with an octane number as high as 115. It is called *neo-hexane*. Its reaction of formation is written as follows:

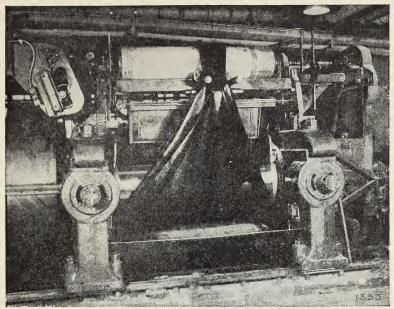
This process uses ethylene which is produced in large amounts from the cracking process. The large-scale production of neohexane will serve as a great conservation industry.

From our present knowledge we assume that molecules with branch chains have higher octane numbers than do those with straight chains. When straight chain molecules are sent through the cracking process some of them break apart and are reformed as branched molecules. This raises the octane value of the resulting gasoline.

Coal Tar Compounds from Petroleum. Now that we are surrounded with wars it pleases us to know that at least one petroleum refiner is prepared to produce toluene from the unsaturated hydrocarbons in cracking gas. It is estimated that this country could easily produce 27 billion pounds of T.N.T. from the toluene thus formed each year. Other compounds such as phenol and xylene, which heretofore have been produced only from coal tar, may also be made from this source. The reactions by which these substances may be formed are not understood.

Unsaturated Compounds in Nature. A great many substances which occur in plants and animals are unsaturated like the ethylene compounds. Cottonseed oil contains oxygen in addition to carbon and hydrogen, but it is also unsaturated. It will react with hydrogen in the presence of powdered nickel to give a saturated compound which is a solid instead of a liquid. This is used to manufacture solid cooking fats from vegetable oils. The oils used in paint and varnish are also unsaturated. In these oils, however, there are several sets of double bonds in each molecule. By this we mean that there are several reactive places within each molecule where hydrogen or other substances may add or hook on. When these oils are spread out in the paint or varnish film they react with the oxygen of the air to form a firm dry substance. We say that the paint "dries."

Rubber. Pure rubber is an unsaturated hydrocarbon with the formula $(C_5H_8)_x$. Scientific research has never brought to light the actual size of the rubber molecule, though chemists



Courtesy of the U.S. Rubber Products, Inc.

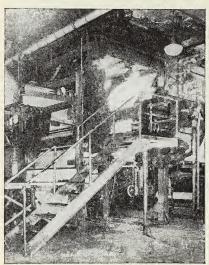
Fig. 97. Rubber Mill

The ingredients are thoroughly mixed by continued rolling.

are sure that it is some multiple of C₅H₈. For instance, it may be C₅₀₀H₈₀₀, but our present methods of investigation do not permit us yet to know. For this reason we use the subscript "x" which here means "unknown times the number." This hydrocarbon is found in many plants, trees and shrubs. However, over 98 percent of the world's supply comes from the rubber tree with its fine-sounding scientific name of *Hevea brasiliensis*. Almost all of the rubber produced comes from cultivated trees.

Rubber trees begin to yield rubber when they are about six years old and continue until they are past forty. Just beneath the bark there are small vessels which contain the rubber as an emulsion. This is called *latex*. It is a milky white fluid which contains small droplets of the hydrocarbon dispersed in a watery serum. The droplets are kept separate by the presence of certain nitrogen compounds which act as a *pro-*

tective colloid. The trees are "tapped" by cutting a layer of bark from the tree and collecting the small amount of latex which oozes out each day. All of the latex is taken to central stations where it is either converted to "crepe" or sold directly. The crepe is formed by diluting the latex with water



Courtesy of the U.S. Rubber Products, Inc.

Fig. 98. Covering Cords with Latex

This forms a rubber-covered cord fabric without cross threads.

followed by dilute acetic acid. This causes the rubber to separate in the form of a doughlike mass which is white when pure. After thorough washing, the rubber is baled for the market. In order to ship latex it is necessary to add ammonia to the product from the trees so that fermentation and separation of the rubber will not take place. Large amounts of latex are now shipped by steamers.

Raw rubber changes with the weather. It gets brittle when cold and sticky when hot. This is

overcome by heating the rubber with sulfur; a process known as vulcanizing. This may be done with the crepe rubber or with such things as gloves shaped by dipping forms into the latex. Rubber absorbs sulfur in quantities up to 30 percent of its weight, and it is probable that much of this actually reacts chemically with the unsaturated hydrocarbon. For soft rubber the sulfur content is as low as 5 percent. Hard "ebonite" results when the larger amounts of sulfur are added. The vulcanizing process with sulfur alone may require several hours of heating. This has been shortened to minutes by the use of catalysts called accelerators. Frequently these bring about the process too rapidly and other catalysts, called accelerator re-

tarders, must be added in order to slow up the vulcanization. During manufacture the amounts of these are controlled exactly.

Most rubber goods contain several things besides rubber and sulfur. Treads for automobile tires contain about 30 percent of carbon black which not only acts as a filler to save rubber but it actually increases the wearing quality of the finished tire. Small amounts of zinc oxide increase the toughness of the tire also. Other substances may be added to give the proper color. In addition to everything else present there is always a small amount of an *antioxidant* put in to decrease the deterioration of the rubber in the air.

Long years of investigation have made it appear that natural rubber is a *polymer* of the unsaturated hydrocarbon *isoprene*. By this we mean that it has been formed by the union of a large number of isoprene molecules to form large molecules which are rubber. This may be represented in part by an equation.

This polymer of isoprene is able to react with another molecule of isoprene or with another molecule like itself. This seems to continue on and on until a molecule with a molecular weight of as much as 150,000 is formed. The rubber molecules which result are still unsaturated and are capable of undergoing many chemical changes. This is shown by the destructive action of air and acids on rubber. The vulcanization with sulfur may well be a union of sulfur with the unsaturated spots in the molecules.

Synthetic Rubber. About 1923 rubber was selling at more than \$1.00 a pound. This gave impetus to the search for a rubber substitute or for a method of making rubber from easily obtained materials. Prior to 1918, in Germany, they tried to make rubber artificially from two unsaturated hydrocarbons:

These are fairly easily obtained, low-boiling liquids. When treated in the proper way each of them polymerizes (large numbers of molecules go together to form very large molecules). The rubber so made was of a very poor quality, and, after rubber prices dropped to about 20 cents a pound, there was little reason to try making a better product. In 1932 an American firm announced the production of a new synthetic rubber, now called "neoprene" (formerly Duprene). This substance is made from acetylene. The acetylene is produced by treating calcium carbide with water. The calcium carbide is produced by heating limestone with coke. The only other substance which actually takes part in the change is hydrogen chloride (made from salt). The product costs too much at present to compete on a cost basis with natural rubber, but there are many uses for which it is far superior to rubber and hence where the extra cost is worth it. It has almost all the properties of rubber but it resists the action of oil much better. Most rubber swells quite a bit in the presence of oil, while this synthetic material swells very little. This has resulted in its use in automobile manufacture, in gasoline hose, in rubber belting for machinery, and in hundreds of other places. It is

claimed to fill a need of its own rather than merely serving as a rubber substitute.

In April, 1940, the Standard Oil Company of New Jersey announced that they would build a plant at Baton Rouge, La., for the production of an artificial rubber. It will operate under a German patent and expects to start making 10,000 pounds of "rubber" daily before the end of the year. The rubberlike material which they will produce is termed "Perbunan" or sometimes "Buna N." It is derived from an unsaturated hydrocarbon, produced from petroleum, called *butadiene*. Its formula as already given is

H. H.

 $H_2C = C - C = CH_2.$

This is allowed to react with another compound called *acrylic nitrile*. Its formula is

 $H_2C = C - C \equiv N.$

These two substances are emulsified in water and mixed under the proper conditions of temperature and pressure. The product of their reaction resembles the ordinary latex of raw rubber and is handled in the same manner as is latex. It is understood that one large rubber company has agreed to take the entire output of the Baton Rouge plant.

The Firestone Tire and Rubber Company has announced that they will produce Buna rubber for its needs in a plant which they have undertaken to build. The B. F. Goodrich Company is now making tires using a synthetic product which they choose to call "Ameripol." It is made from butadiene together with another compound which they do not see fit to reveal. They admit that the other product is made from natural gas and air. These are treated in much the same way as in the formation of "Buna N." Tires made from this material cost more than those made of natural rubber.

When first attempts were made to produce a synthetic rubber it was intended thereby to replace natural rubber. The price of rubber varies so that this would be hard to do. With the production of synthetic "rubber" an accomplished fact, their properties have been studied. Many times they are far superior to natural rubber for certain purposes. Truck and tractor tires may now be made with oil-proof treads. Engines may be mounted on rubber to cut down vibration. We are confronted with a need of a source of rubber which is not controlled by a foreign monoply. Our present beginning may well lead to our complete independence with regard to rubber supplies.

Acetylene. Acetylene, to which we have referred several times, is a combustible gas. When burned with oxygen in a special oxyacetylene blowtorch it produces an extremely hot flame used in the welding and cutting of steel. It is made by dropping water onto lumps of calcium carbide.

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$
 (acetylene)

We may readily see that the molecule of acetylene has four hydrogen atoms less than the molecule of ethane (C₂H₆). With hydrogen in the presence of a catalyst acetylene will react to form, first, ethylene and then ethane. Because of this great unsaturation we find that acetylene is quite reactive chemically. In the presence of certain mercury salts it will even react with water to form a substance known as acetaldehyde.

$$C_2H_2 + H_2O \rightarrow C_2H_4O$$
 (acetaldehyde)

From acetaldehyde may be made scores of different substances. Altogether there are more than 300 different industrial chemicals produced from acetylene. We have already mentioned its use in the manufacture of artificial rubber. The new synthetic fiber (nylon) which has been so widely discussed in the daily papers as a material for making stockings like silk is also made by using acetylene.

We may account for the chemical activity of acetylene as we did for the activity of ethylene. We find that there are not enough electrons "to go around" unless we let the two carbon atoms share six between them. This is represented as follows:

:
$$H:C:C:H$$
 or $H-C \equiv C-H$

These extra electrons may be shared with other elements with which acetylene may react. For example, chlorine reacts with acetylene so rapidly that an explosion results when the two gases are mixed.

$$H-C \equiv C-H + 2Cl_2 \rightarrow H-C-C-H \text{ (acetylene tetrachloride)}$$

$$Cl Cl Cl$$

As would be expected, there is a homologous series of compounds like acetylene. The other members of this series do not as yet have the industrial uses that acetylene has, however.

Benzene Hydrocarbons. There is another class of hydrocarbons which comes mainly from the distillation of coal tar. The most common representative of this group of substances is benzene which has the formula C₆H₆. For many years, prior to 1865, chemists were puzzled in their attempts to write a structural formula for this substance. At that time a German, named Kekulé, offered a possible solution which is still used. He imagined the six carbon atoms of the benzene molecule as being tied in a circle. Attached to each carbon atom was one hydrogen atom. Thus all of the carbon atoms were in a ring which has become known as the benzene ring. This may be represented as follows:

Since we think that the valence of carbon must always be four, it is necessary to assume that benzene is unsaturated. This is shown by the electronic structure or by the use of "double

bonds." The chemical behavior of benzene bears out the unsaturation which was assumed. The complete formula for the compound is usually written as:

but chemists get in a hurry and sometimes they leave out the symbols of the elements which make up the compound. The chemist writes benzene as:

This symbol in combination with crossed retorts is the emblem of the Chemical Warfare service.

There is a whole series of substances which are chemically like benzene and these are known as the *benzene hydrocarbons*. These, also, differ from each other by CH₂ in their formulas and thus they form a homologous series. Since many of these compounds have a peculiar odor they are also termed *aromatic hydrocarbons*. A few of them are drawn in structure form.

All of these are important solvents. The last four structures show the possible isomers with the formula C₈H₁₀. All of these are known.

SUMMARY

The compounds of carbon are termed organic compounds. Many of these are essential to life. Carbon atoms may combine with other carbon atoms as well as with other elements. The resulting molecules may be quite complex.

The hydrocarbons may be classified in homologous series the members of which differ from each other by CH₂ in their formulas. A few of these are the methane, ethylene, acetylene,

and benzene series.

Members of the methane series are called saturated hydrocarbons. They are characterized by a relatively low chemical activity. Members of the ethylene and acetylene series are said to be unsaturated. They are characterized by a high chemical activity. Members of the benzene series possess molecules containing a ringlike connection between the carbon atoms. These, too, possess a certain degree of unsaturation and a high reactivity.

Hydrocarbons, as well as compounds made from them, may exist as straight chain and branched chain isomers. The enormous number of hydrocarbons is accounted for in this manner.

Petroleum hydrocarbons are largely saturated, but may be partially converted to unsaturated substances by cracking.

Many unsaturated compounds exist in nature as plant and

animal products.

Rubber is an unsaturated hydrocarbon which occurs in certain plants as latex. It reacts with sulfur to become vulcanized. Articles of rubber contain antioxidants to prolong their life.

Natural rubber is a polymer of isoprene. Synthetic rubber may be made from acetylene, butadiene, isoprene, and ethylene. Recent indications point toward a considerable production of such material in the United States.

REVIEW QUESTIONS

- 1. Why is it possible for so many hydrocarbons to exist?
- 2. Why are carbon compounds called organic?
- 3. What relationship exists between members of a homologous series?
 - 4. Why are members of the methane series called paraffins?
- 5. Distinguish between saturated and unsaturated hydrocarbons.
- 6. What type of valence forces operate within hydrocarbon molecules? How do these differ from that within the sodium chloride molecule?
- 7. How do we account for the existence of two or more hydrocarbons with the same analytical formulas (derived from analysis)?
 - 8. Is it true that ethylene causes bananas to ripen faster?
- 9. How do we account for the great chemical reactivity of ethylene?
- 10. What chemical fact makes possible the formation of polymer gasoline?
- 11. For what apparent reason does the cracking process raise the octane rating of gasoline?
 - 12. Why is it possible for rubber to react with sulfur?
- 13. Rubber must be treated to prevent destruction by the air. Account for this.
- 14. Why is it possible for artificial rubber to be sold at a price which is higher than the price of natural rubber?
 - 15. How is acetylene made? Give some of its uses.
 - 16. What is peculiar about the formula for benzene?

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DERIVATIVES OF THE HYDRO-CARBONS

The compounds which may be made from the hydrocarbons are even more important than are the hydrocarbons themselves. By means of chemical changes it is possible to remove one or more hydrogen atoms from the different hydrocarbons and in the place of the hydrogen to put other atoms or groups of atoms. In this manner it is possible to make many thousands of different substances. These new things are said to be derivatives of the hydrocarbons even though the same substance may occur in nature. The study of the hydrocarbons and the things which may be made from them is called organic chemistry. In general the name has been applied to the study of all the compounds of carbon wherever and however they may be obtained. There are more than 300,000 such compounds known, and many others are prepared each year. Some of our greatest industries are confined to the manufacture of products made entirely from the compounds of carbon. These industries depend upon chemical changes which may be brought about and which result in the conversion of one compound into another. There is so much to the chemistry of the organic substances that it would be next to impossible to remember much of it save for the fact that most of the compounds may be classed into large groups of similar things. In a general way all of the members of these similar groups behave alike and the chemist soon learns to rely upon these generalities. A few of the more common of these groups will be discussed. The grouping is done according to the other elements or groups of elements which may be present.

Compounds with Chlorine. We shall illustrate some of

these types of compounds by means of changes brought about in the paraffin hydrocarbons. If methane is treated with chlorine in the presence of sunlight the chlorine is able to replace the hydrogen atoms one at a time.

 $\begin{array}{c} CH_4 + Cl_2 \rightarrow HCl + CH_3Cl & methyl \ chloride \\ CH_3Cl + Cl_2 \rightarrow HCl + CH_2Cl_2 & methylene \ chloride \\ CH_2Cl_2 + Cl_2 \rightarrow HCl + CHCl_3 & chloroform \\ CHCl_3 + Cl_2 \rightarrow HCl + CCl_4 & carbon \ tetrachloride \\ \end{array}$

Methyl chloride has long been used as the liquid in mechanical refrigerators, but, since it has a toxic (poisonous) effect, and has caused severe illness in persons exposed to a leaky machine, other liquids such as sulfur dioxide, ammonia, and "Freon" are being used more and more. Chloroform is well known as an anesthetic. But this, too, is dangerous to human health and life if used for long periods of time, and, in consequence, chemists, anesthetists, and surgeons continue experimenting to find better anesthetics. Carbon tetrachloride finds many uses because it will not burn. Cleaning fluids containing the proper amount of carbon tetrachloride are efficient as dry cleaners and have almost no fire hazard. As the liquid in certain fire extinguishers (Pyrene) it finds sale for putting out small fires. This it does by forming a blanket of heavy vapor over the fire and shutting out the air. The use of carbon tetrachloride is accompanied by some danger, since it has a poisonous effect if breathed for some time. When used properly in the presence of fresh air, and if the fumes are not inhaled, there seems to be no danger involved.

A certain compound containing both chlorine and fluorine (CCl₂F₂) is unusual in that it is not harmful even if breathed for a considerable time. This substance, called dichlorodifluoromethane, is sold under the trade name of "Freon" for use as the liquid in refrigerating machines. Other properties which it possesses, such as ease of evaporation, the large amount of heat absorbed while evaporating, and the ease of condensing it to a liquid, make it the most desirable fluid for this purpose.

From other hydrocarbons it is possible to make still other

chlorine compounds and many of these find considerable use. Sometimes compounds containing chlorine cannot be made in pure form by the action of chlorine with the hydrocarbon, and it becomes necessary to use some indirect method to accomplish the desired result. If the gas ethylene is treated with hydrogen chloride (HCl) we get ethyl chloride.

This substance is used in the manufacture of lead tetraethyl, which is the ethyl fluid in gasoline. To make this, ethyl chloride is treated with an alloy of sodium and lead. The sodium reacts with the chlorine of the ethyl chloride while the remaining portion of the molecule combines with lead.

$$\begin{aligned} 4C_2H_5Cl \,+\, Na_4 \!\cdot\! Pb &\rightarrow 4NaCl \,+\, Pb(C_2H_5)_4 \\ &\quad \text{lead tetraethyl} \end{aligned}$$

If ethylene is treated with bromine it forms ethylene dibromide.

Ethylene dibromide is important because it must be mixed with all gasoline which contains lead. When lead tetraethyl burns in an engine the lead is set free and much of it may be ejected from the exhaust as a fine powder. If this floats about in the air there is danger of its causing lead poisoning. This danger is removed by mixing the proper amount of ethylene dibromide with the leaded gas. When this burns it liberates free bromine in intimate contact with the lead. These react to form lead bromide which is a heavy powder. Some of this is

deposited along the exhaust and muffler. That which gets into the air should soon settle to the ground though it is harmless.

By treating ethylene with chlorine we get ethylene dichloride.

This substance is used in the manufacture of certain types of synthetic rubber and synthetic resins. Notable among these is "Thiokol."

If acetylene is treated with chlorine we get a reaction similar to that with ethylene though in this case it takes place twice.

This reacts with additional chlorine.

The above reactions by which one molecule of a reactive substance combines with a molecule of the unsaturated compound are called addition reactions. These are typical of all unsaturated compounds.

The compounds of the hydrocarbons with chlorine and bromine are heavy liquids with considerable solvent ability. They are sometimes used in the purification of lubricating oil. Because they do not catch fire easily these solvents are used to extract plant oils from plant tissue. The pyrethrum extract used to kill flies and other insects is so obtained. Soy bean oil is sometimes extracted from the meal by the use of these solvents. A number of serious fires and explosions have resulted from the use of inflammable solvents for these purposes.

Radicals. When another element such as chlorine is introduced into a hydrocarbon molecule in place of a hydrogen atom, it is this new element which usually gives the most characteristic properties to the substance which is formed. The unchanged part of the molecule merely tags along and may go through many chemical reactions unchanged. This remaining hydrocarbon-portion of the molecule is called a *radical*. Radicals are named in a systematic manner which depends upon the hydrocarbon involved. A few examples will make this clear.

Hydrocarbon		Compound		Radical
CH_4	methane	CH ₃ Cl	methyl chloride	CH ₃ — methyl
C_2H_6	ethane	C_2H_5Cl	ethyl chloride	C_2H_5 — ethyl
C_3H_8	propane	C_3H_7Cl	propyl chloride	C ₃ H ₇ — propyl
C_4H_{10}	butane	C_4H_9Cl	butyl chloride	C ₄ H ₉ — butyl

Because of the very complex nature of some organic compounds it has been necessary to devise a strict system of naming them to keep them all straight in the chemist's mind. This system has been accepted by international agreement of scientists. The possibilities for different isomeric compounds is so great that without such a system the name given to a compound by one chemist would mean nothing to any other laboratory worker.

The Alcohols. If the chlorine compounds listed above, as well as other similar ones, are treated with a water solution of sodium hydroxide (caustic soda) the chlorine will be replaced by a hydroxyl (OH) group.

$$\begin{array}{l} CH_3\overline{Cl+Na}OH \rightarrow NaCl+CH_3OH \ \left\{ \begin{array}{l} methyl \ alcohol \\ wood \ alcohol \end{array} \right. \\ C_2H_5\overline{Cl+Na}OH \rightarrow NaCl+C_2H_5OH \ \left\{ \begin{array}{l} ethyl \ alcohol \\ grain \ alcohol \end{array} \right. \end{array}$$

This new type of compound is called an alcohol. The two alcohols shown are the most important to human beings. While these two alcohols are not prepared by the method indicated

in the equations since it would cost entirely too much to carry out the process, the chemical equations do show the relation of the alcohols to the hydrocarbons.

Methyl Alcohol. Until a few years ago all of the methyl alcohol used was obtained as a by-product of the distillation of wood in the manufacture of charcoal. The material so obtained was commonly called wood alcohol. There have been many cases reported in which men have drunk wood alcohol with the idea that anything named alcohol was made for that purpose. The result is usually death or blindness. An attempt is being made to change the name from alcohol to "methanol" in keeping with good chemical usage and to keep the ignorant from disaster. It is this name which industry is now successfully using for the product. About 1923 a process was developed in Germany for the production of methyl alcohol synthetically. When a mixture of carbon monoxide and hydrogen (water gas) is brought in contact with a suitable catalyst at a temperature of about 400° C. and under pressure of 50 atmospheres methyl alcohol is formed.

$$CO + 2H_2 \rightarrow CH_3OH$$

A mixture of the oxides of zinc and copper serves as a catalyst for this reaction.

The production of synthetic methyl alcohol costs much less than its production by wood distillation. This has resulted in severe competition for the wood distillation industry. In fact, it is threatened with complete extinction. During 1939 the U. S. production of synthetic methyl alcohol amounted to about 34,000,000 gallons and this was 89 percent of the total production in this country.

Uses of Methyl Alcohol. The largest uses for methyl alcohol are:

1. Denaturing ethyl alcohol in order to free it from beverage taxes. Completely denatured ethyl alcohol contains 10 percent of methyl alcohol but is satisfactory for certain chemical manufacturing processes.

2. Antifreeze for automobile radiators. It takes fewer

pounds of methyl alcohol to protect a radiator against freezing than it does of any other such product. This is due to the low molecular weight of this compound (see Chapter 7).

3. Solvent for shellac and varnish. A large amount of the stuff which comes in the can of varnish is nothing but a solvent to keep the actual varnish in a liquid state. When the varnish is spread out on a surface the solvent evaporates and leaves the dissolved material in the form of a firm dry coating.

4. The production of formaldehyde to be used as a disinfectant in hospitals or in the production of "Bakelite" and other similar resins. These resins are seen daily in such articles as telephones, pencils, ash trays, cases for clocks, backs for hair brushes, steering wheels for automobiles, and

switch buttons for radios.

Ethyl Alcohol. Ethyl alcohol (grain alcohol, beverage alcohol, ethanol) has been produced by the fermentation of fruit sugar and grains since the earliest times of history. The relationship between the molecule of ethyl alcohol and the molecule of ethane is shown by the fact that ethyl alcohol can be produced from ethyl chloride.

It is far too much trouble to try to make ethyl alcohol by this method because there are much easier ways.

Synthetic Ethyl Alcohol. It has been mentioned that the

process of making gasoline by cracking petroleum products results in the formation of large amounts of ethylene ($CH_2 = CH_2$). The addition of the elements of water as (H–OH) to the ends of the double bond in ethylene results in the formation of ethyl alcohol.

Ethylene is passed into sulfuric acid and then water is added to the resulting compound. Ethyl alcohol is produced and its cost of production is low enough to compete with alcohol from the fermentation industries. The cost of getting back the sulfuric acid used keeps this ethyl alcohol from being even cheaper than it is.

Alcohol by Fermentation. The largest production of ethyl alcohol in this country is from the fermentation of "black strap" molasses. This material is purchased from the Cuban sugar mills and contains that part of the sugar syrup which will not crystallize as sugar. The chemical change which takes place during fermentation may be written as:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 4C_2H_5OH + 4CO_2$$

sugar ethyl alcohol carbon dioxide

The reaction equation does not indicate in any way just how the process occurs. It was Louis Pasteur who first discovered that the process of fermentation is due to the presence of certain plant organisms which exist upon the skins of fruit. At first it was supposed that the organism utilized the sugar as food and secreted the alcohol and carbon dioxide as waste products. It has been shown, however, that it is not the living organism which brings about the change, but instead it is a substance produced during the growth of the organism which acts as a catalyst for the change.

The organism which causes fermentation is known as yeast.

It is a vegetable growth. Within the yeast cells there are certain complex substances which may serve as catalysts for chemical changes. These catalysts are known as enzymes. If the yeast cells are destroyed by grinding or crushing the resulting material will produce fermentation just the same as the yeast itself. In actual practice it is neither necessary to grind the yeast nor to isolate the enzyme. The yeast is simply allowed to grow within a solution containing the sugar to be fermented. In order to grow, the yeast uses some sugar along with certain mineral salts, phosphates, and nitrogen containing material. As a rule the yeast is grown outside the fermentation vats and is added to the sugar solution in amounts great enough to bring about the fermentation in as short a time as possible. The alcohol is distilled from the resulting "mash" by means of steam. Repeated distillation of the alcohol so obtained brings about a partial separation from the water which also distills but this cannot be carried out to produce higher than 95 percent alcohol.

In certain foreign countries alcohol is produced from starch by a fermentation process. In this case it is first necessary to change the starch to a material which can be fermented. This change may be brought about by another enzyme, called *diastase*, which occurs in grains of barley during sprouting. Barley is sprouted in a warm, damp atmosphere until the sprouts are well formed. The sprouted grains are heated just hot enough to stop the growth but not to destroy the diastase. The resulting material is called "malt." Starch from various grains or potatoes is changed to a sugar called *maltose* if treated with this malt in the presence of water. After the maltose is formed it is fermented to form alcohol by means of yeast.

In 1939 the United States produced 221,617,741 proof gallons of ethyl alcohol. A proof gallon is a gallon containing 50 percent alcohol in water. This was produced from molasses, corn, rye, barley, ethylene, waste from paper mills, pineapples, potatoes, and wood pulp.

Uses of Alcohol. The uses of ethyl alcohol are so great that it must be classified as a necessary chemical. It is a necessary

solvent for perfumes since no suitable substitute has ever been found. Certain flavoring extracts require alcohol as a solvent (vanilla). We find it, too, as a solvent in the industries which make and use lacquer, celluloid, smokeless powder, varnish, shellac, and enamel. It is an important fuel for automobiles in countries not having large supplies of petroleum. Alcohol is a convenient substance to use in the preparation of other compounds. Chloroform is prepared from it. More than a third of the alcohol produced in this country is denatured for use as an antifreeze in automobiles.

Alcoholic beverages contain ethyl alcohol. When taken into the body the ethyl alcohol is converted into carbon dioxide and water by the normal body process. This process is not rapid and the excess alcohol which may be consumed is soon found in the blood stream. It is this alcohol in the blood which causes the dullness of the brain and other effects which in the extreme are associated with drunkenness. When the body is overtaxed with alcohol the normal burning to carbon dioxide is incomplete and acetic acid is formed. Continued use of alcohol as a beverage produces serious effects of a chemical nature which are best discussed in a course on physiology. The matter of overuse of alcohol has not been properly studied. There is some evidence which indicates an actual condition of disease in many cases.

Prestone. The alcohols which have been discussed have only one hydroxyl group in their molecules but there are other alcohols with more than one such group. One of the most important of these alcohols is the one called *ethylene glycol*. It contains two carbon atoms and two hydroxyl groups in each molecule. The accepted formula is written as:

It finds its greatest use as an antifreeze for automobiles under the name "Prestone." It is produced from the gas ethylene which is a by-product of the cracking of petroleum. By treating ethylene with chlorine gas in water we get ethylene chlorohydrin.

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

$$H \qquad H \qquad H$$

$$C = C \qquad H + HOCl \rightarrow H \qquad C - C - H$$

$$H \qquad Cl \quad OH$$

$$ethylene chlorohydrin$$

This product when heated with a water solution of sodium bicarbonate (baking soda) is changed to ethylene glycol.

Glycerin. Another alcohol is glycerin.

This is produced as a by-product of soap manufacture. However, there are several additional methods for getting glycerin, and we are not at all dependent upon soap companies for the product. Like the other alcohols this one finds a considerable use as an antifreeze. Since they each have a high boiling point, glycerin and ethylene glycol are alike in that they are not lost from the radiator by evaporation as are methyl and ethyl alcohols. This offsets their higher initial cost to some extent.

Glycerin is harmless to the human body. This is not true for ethylene glycol. If we were to drink "Prestone" the process of digestion would change the ethylene glycol to oxalic acid which is a deadly poison. A few years ago a number of deaths were reported as being due to sulfanilamide which was dissolved in a solvent made from ethylene glycol. The harmless nature of glycerin permits its use in food and medicine as well as in cosmetics of all sorts. Since glycerin absorbs moisture from the air we find it used on shredded cocoanut and prunes in order to keep these products in a moist condition. This same property of glycerin is used in non-drying ink pads which

must stay moist for use with rubber stamps. Glycerin is extremely widespread in nature, since all of the plant and animal fats and oils are compounds of it.

Ether. The discovery of the anesthetic value of ether was a great boon to modern surgery. When ether and other anesthetics are breathed, they pass into the blood stream and produce numbness of the nerves. The effect is that of a deep sleep so that the surgeon's knife is not painful as it cuts the flesh.

When sulfuric acid is heated with relatively large amounts of ethyl alcohol ether is produced. This is really due to the removal of water from the alcohol.

The process is carried out on a large scale. In a normal year about 8 million pounds of ether, which is suitable for medical purposes, is produced in the United States. In addition to this there are other large amounts of this substance produced for use as solvents.

Other Anesthetics. A number of substances are capable of producing the deep sleep of anesthesia. Chloroform (CHCl₃) is one of the oldest but it must be used with great care to prevent poisoning. One of the newer anesthetics is ethylene (CH₂ = CH₂). This substance produces a deep sleep when used with oxygen, and none of the bad effects of ether are noticed. The patient wakens without either nausea or a feeling of depression. The effect upon the heart does not appear harmful, and thus it is used with older persons with great success. For many years the dentist has used "laughing gas" or nitrous oxide (N₂O) to put a patient to sleep for a short while. The effects of this gas soon disappear. Nitrous oxide is used frequently before giving a patient ether in order to prevent his usual struggle against the going into anesthetic sleep.

Aldehydes. A class of substances known as aldehydes may be produced from alcohols. Some of these aldehydes such as *formaldehyde*, from methyl alcohol, and *acetaldehyde*, from ethyl alcohol, are quite important.

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Formaldehyde. Formaldehyde is produced from methyl alcohol by passing hot air through the alcohol contained in a copper vessel. The oxygen of the air, in the presence of the copper which serves as a catalyst, combines with a part of the hydrogen in the alcohol.

$$\begin{array}{c|c} H & H \\ | & | \\ H-C-OH+O \\ \hline \\ H & \end{array} \rightarrow \begin{array}{c} H-C=O+H_2O \\ \\ \text{formaldehyde} \end{array}$$

Formaldehyde is quite soluble in water and the water solution (40%) is sold as "formalin." This is used as a disinfectant. A large amount of formalin is used to combat plant diseases such as potato scab and the "damping" of seedling plants in green houses. Formaldehyde is also used as an insecticide, as an embalming fluid in preparing corpses for burial, and as a hardening agent for animal protein. When the curd from milk (casein) is treated with formaldehyde it becomes quite hard. Thus it becomes possible to make buttons and billiard balls from milk. The greatest amount of formaldehyde is used in the production of synthetic resins such as "Bakelite."

Acetaldehyde. The careful treatment of ethyl alcohol with oxygen produces acetaldehyde.

Just as in the case of formaldehyde we see the formula of this substance has in it the group | which is said to be char-

acteristic of aldehydes. It is an extremely reactive group chemically and a lot of things may be made from the aldehydes because of the ease with which they take part in chemical reactions. From acetaldehyde may be made a very valuable sleep producing compound known as paraldehyde.

The demand for things produced by means of acetaldehyde is so great that this substance is made in large amounts from cheap materials. If we look at the formula of acetylene ($HC \equiv CH$) we can see that by adding H_2O we will have the formula for acetaldehyde. Acetylene is passed through water containing a mercury compound and acetaldehyde is formed. The acetylene is produced by the action of water upon calcium carbide which in turn is produced from limestone and coke. A large amount of the acetaldehyde produced is converted to acetic acid which is used in the production of non-explosive motion picture film especially in 16 mm or 8 mm sizes for home amateur movie cameras, and certain types of rayon.

Acids. When the alcohols or the aldehydes are oxidized, otherwise than by burning, they are changed to acids. These are called *organic acids* and they are found widely distributed in nature.

Formic Acid. When either methyl alcohol or formaldehyde is treated with strong oxidizing agents formic acid is produced.

$$\begin{array}{c|c} H & OH \\ \hline | & \\ H-C = O + O \rightarrow H-C = O \\ \hline \text{formic acid} \end{array}$$

This acid was first made by the distillation of the bodies of red ants. The acid which distilled was called "ant acid" and that is what the name "formic acid" means. There are so-called stinging nettles which also contain formic acid. This acid produces severe blisters and swelling when left in contact with the skin.

Acetic Acid. The oxidation of acetaldehyde produces acetic acid.

$$\begin{array}{c|ccccc} H & H & & H & OH \\ & & & & & | & | & | \\ H - C - C & = & O & + & O \rightarrow H - C - C & = & O \\ & & & & | & & | \\ & & & & H & & H \end{array}$$

This acid was known long ago since it occurs in vinegar to which it gives the acid properties. In 1939 the United States produced 215 million pounds of acetic acid. About one fifth of this was produced from the distillation of wood. The remainder was made largely by synthetic methods. The two outstanding methods are the addition of water to acetylene to form acetaldehyde followed by its oxidation, and the oxidation of alcohol by means of air and bacterial action.

Vinegar. Vinegar is usually produced from fruit juices though it may be made from any dilute solution which contains from 12 to 16 percent of sugar. The first step in the process is the conversion of the sugar to alcohol by the process of fermentation with yeast. The yeast is already present on fruit and some of it gets into the juice. After the alcohol is formed it may be converted to acetic acid by the action of oxygen from the air in the presence of a microorganism called *Bacterium aceti*. The fermented fruit juice is placed in kegs to which air is admitted. The *Bacteria aceti* form films which are called *mother of vinegar* and this is usually best obtained from another batch of vinegar. Vinegar so made is not ready for use until the action has been going on for several months. Most fruit juices produce a vinegar which is about 5 percent acetic acid though some is a little stronger than this. The food laws require that the vinegar sold shall contain not less than 4 percent of acetic acid.

Quick Vinegar Process. Now that the manufacture of vinegar is on a commercial basis it is necessary to speed up the time required for the conversion of fruit juice to acetic acid. This is accomplished by increasing the availability of the oxygen which enters the reaction. The fruit juice is fermented in the usual manner and the dilute alcohol solution is allowed to trickle down over tasteless beechwood shavings which have been covered with mother of vinegar. An ample supply of air is made available. The action requires only a few days and the vinegar is satisfactory. Some manufacturers use dilute alcohol for the process in place of fruit juices and their product is usually sold as "sugar vinegar."

Acetic acid produced in this manner is always too dilute to use in other industries though there are methods for its concentration. The largest single consumer of this acid is the manufacture of cellulose acetate. This requires 100 percent acetic acid as a starting material. Cellulose acetate is used in non-explosive motion picture film and in the type of rayon known as *celanese*.

Esters. Organic acids will react with alcohols to give compounds which may be compared with salts. They are called *esters*. This reaction is typified by the formation of an ester with ethyl alcohol.

$$\begin{array}{c} O \\ CH_3C \stackrel{\frown}{\longrightarrow} OH \\ \text{acetic acid} \\ \end{array} + \begin{array}{c} C_2H_5OH \\ \text{ethyl alcohol} \\ \end{array} + \begin{array}{c} O \\ CH_3C \stackrel{\frown}{\longrightarrow} O \\ -C_2H_5 \\ \text{ethyl acetate} \end{array}$$

There are many esters known. Some are found in nature in the form of oils. Oil of wintergreen is *methyl salicylate* which may be produced from methyl alcohol and salicylic acid. Natural fats are esters of glycerin with long chain acids known as "fatty" acids. Butter contains the ester of glycerin and butyric acid. It is the decomposition of this compound into butyric acid which causes butter to have a bad odor when it gets old. *Ethyl butyrate* is the essential flavor in the pineapple and this substance is used as an artificial flavoring. *Isoamyl acetate* is used to prepare artificial pear essence. Persons who know and like wines will pay a premium price for one which has a special "bouquet." This is produced by a minute quantity of certain natural esters of amyl and ethyl alcohols with small amounts of acids which are present.

The esters are among our most important solvents. Ethyl acetate and butyl acetate are particularly useful in the preparation of lacquers. These esters serve to dissolve the resinous material of which the lacquer is composed and they evaporate after it has been spread. Some of the higher boiling esters are mixed with artificial resins and artificial rubber as internal lubricants called plasticizers. They do not evaporate but remain in the body of material keeping it pliable.

Perfumes and Flavors. Mankind has long desired the pleas-

ant effects of certain perfumes and flavors. We are told that most of our flavor of food is noticed by way of our noses. We used to believe that only nature could prepare those rare combinations of substances which we find in the rose, the violet, the jasmine, and the orange blossom. Any attempts of men to duplicate these were to be classed as pure artificiality and a fraud. Chemists have not been so easily discouraged, and some of the greatest among them have dared to find out the chemical nature of these materials. Some of these natural odors have been made in the laboratory, and now the chemist is an essential part of the perfume industry.

The principal ingredient of attar of roses is geraniol, an

unsaturated alcohol.

By careful oxidation this may be converted to an aldehyde with the same molecular arrangement. It is called citral.

$$CH_3$$
 H H CH_3 H
 CH_3 — $C = C$ — C — C — C — $C = C$ — $C = O$
 CH_3 — C

This is the odor in lemons, oranges, and verbena flowers.

The particular odor of rose water is given by almost pure phenyl ethanol.

The essential odor of violets is due to a substance called *irone*.

The great American flavor is that from the vanilla bean which the chemist calls *vanillin*. It is a derivative of phenol and has the formula:

It is easily prepared and is many times stronger than the natural product. This is found in nature together with another substance called coumarin which has a most pleasant odor. Its formula is:

This substance is used with vanillin in the preparation of artificial vanilla flavors. In perfumes coumarin gives the odor of "new mown hay."

It is not intended to give the idea that good perfume may be made in the laboratory by direct synthesis. The chemist is able to make most of the substances to which perfumes owe their fragrance but he is not necessarily able to produce the exact odor. This is accomplished by blending correct amounts of many different odors. Just as the musical artist may blend a hundred instruments and the color artist may blend his shades of color, the perfume artist may blend a dozen substances to give his symphony of odor. The chemist cannot displace the perfumer. He furnishes better and cheaper products with which the perfumer may practice his art.

War Gases. Because of the trend of the times it may be well to give brief mention to the war gases. According to the Chemical Warfare Service there are four types of gases based upon their physiological action.

1. Lung injurants. These are substances which cause inflammation and injury to the interior cavity of the breathing organs. Examples are *phosgene* and *chlorpicrin*.

2. Irritants (sternutators). These are substances which produce violent sneezing and coughing. They cause a period of temporary physical disability. An example is diphenylchlorarsine.

Cl—As
$$C_6H_5$$

The peculiar effects seem to be caused by the atom of arsenic.

3. Lachrimators. These are substances which produce a copious flow of tears and intense eye pains. The effects are temporary. Examples are bromacetone, brombenzylcyanide, and chloracetophenone.

4. Vesicants. These are substances which, when absorbed or dissolved in any part of the body, produce burns with destruction of the tissues. Examples are mustard gas and lewisite.

The most deadly of all are mustard gas and lewisite. They are not gases but are high boiling liquids. Wherever droplets of them touch the clothing they will serve as sources of destruction. They penetrate clothing and even rubber. Their presence in contact with the skin is just as bad as breathing them. The ground where these gases have been used is dangerous to human beings for many days afterward or until it has been treated with alkaline material.

SUMMARY

Substances which may be produced by substituting another element or group of elements for the hydrogen atoms in hydrocarbons are called derivatives of the hydrocarbons. The particular element or group of elements so substituted determines the class into which the derivative is placed.

The most common classes discussed are the chlorine derivatives, the alcohols, the aldehydes, the acids, the esters, and the ethers. These are related in that the chlorine compounds

may be made from the hydrocarbons and the others may be

prepared from them.

The chlorine compounds are important solvents and chemical reagents. The alcohols are solvents, antifreeze substances, and sources of compounds through chemical change. The aldehydes are substances from which other things may be made. Acids are greatly used as reagents in the manufacture of salable articles. Esters are used as solvents. Ethers are solvents and ethyl ether is an anesthetic.

Perfumes and flavors are derivatives of the hydrocarbons and many of them are made synthetically. The natural products are mixtures.

War gases are classed as lung injurants, sternutators, lachrimators, and vesicants. Most of these are hydrocarbon derivatives which contain chlorine or bromine and, in many instances, arsenic.

REVIEW QUESTIONS

1. What kinds of substances are classed as derivatives of the hydrocarbons?

2. Give some important uses of carbon tetrachloride. Would

you expect chloroform to catch fire easily?

3. What is "freon"? What are its advantages in the field in which it is used?

4. Outline the method for making ethyl fluid. What precaution must be taken by those working with this substance?

5. How do we make sure that no free lead will be ejected from an automobile exhaust?

- 6. What kind of chemical reaction is characteristic of unsaturated hydrocarbons?
 - 7. What are the important uses of the chlorine derivatives?
- 8. What do we mean by organic radicals? Give some examples.
 - 9. Can ethyl alcohol be prepared from ethyl chloride? How?
 - 10. Can ethyl chloride be prepared from ethane? How?
- 11. Give the commercial methods of preparing methyl alcohol. Give its uses.
 - 12. Outline the commercial method of preparing ethyl alcohol.

13. How may ethyl alcohol be made from the gas obtained during the cracking of petroleum?

14. List some of the uses of ethyl alcohol.

- 15. What is prestone? How is it made? For what is it used?
- 16. What is our principal source of glycerin? For what is it used?
 - 17. How is ether made?
- 18. Give some important uses of formaldehyde. What is "formalin"?
 - 19. Describe the process used in vinegar manufacture.
- 20. What are esters? How may they be made? For what purpose are they used?
- 21. Why is it that the chemist is unable to exactly duplicate natural perfumes and flavors?
 - 22. Classify war gases and give their physiological effects.

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FATS. SOAP. SYNTHETIC RESINS

FATS

All of the plant and animal fats and oils which occur in nature are esters produced by the union of glycerin with an acid. As a rule these acids are what we call "long chain" acids since there are frequently 15 to 18 carbon atoms in each acid molecule. The common fat known as butter contains some of the ester known as glyceryl tributyrate.

The acid in this ester contains only 4 carbon atoms in each molecule. The acid itself is known as butyric acid. The fat present in lard is partly the ester formed from glycerin and stearic acid ($C_{17}H_{35}C - OH$).

$$C_{17}H_{35}-C \stackrel{\bigcirc{}/O}{-}CH_{2}$$
 $C_{17}H_{35}-C \stackrel{\bigcirc{}/O}{-}CH$
 $C_{17}H_{35}-C \stackrel{\bigcirc{}/O}{-}CH_{2}$

It is called *stearin*. At room temperature this fat is a firm white solid.

Olive oil is a mixture of various fats. It contains the glycerin esters of stearic acid, palmitic acid ($C_{15}H_{31}C OH$), and oleic acid ($C_{17}H_{33}C OH$). Cottonseed oil contains the glycerin esters of these three acids named above together with the ester of linoleic acid ($C_{17}H_{51}C OH$).

Unsaturated Fats. If we compare the formulas for the four acids just listed we can see that two of them do not have all of the hydrogen which they may contain.

Palmitic acid $C_{15}H_{31}C \stackrel{\bigcirc{}}{-}OH$ saturated solid Stearic acid $C_{17}H_{35}C \stackrel{\bigcirc{}}{-}OH$ saturated solid Oleic acid $C_{17}H_{33}C \stackrel{\bigcirc{}}{-}OH$ unsaturated liquid above 14° C. Linoleic acid $C_{17}H_{31}C \stackrel{\bigcirc{}}{-}OH$ unsaturated liquid above 0° C.

Those molecules which are short of hydrogen are unsaturated and this causes them to be liquids at room temperatures. The glycerin esters of these unsaturated acids are also liquids while the glycerin esters of the saturated acids are solids.

Cooking Fats. This difference in state which is due to unsaturation is noticed particularly in cooking fats. Lard, which is chiefly olein, is a soft solid, and tallow which has a similar composition but contains more stearin is even harder. Olive oil, cottonseed oil, and other vegetable oils which are chiefly esters of the unsaturated acids are all liquids at room temperature. Many women object to the use of animal fats in cooking, and yet they want a solid cooking fat. It is a relatively simple matter to convert the liquid fats into solid fats by means of hydrogen. For instance, the addition of two atoms of hydrogen to oleic acid will produce stearic acid and the addition of four atoms of hydrogen to linoleic acid will produce stearic acid. The unsaturated acids contain double bonds between certain carbon atoms (—C=C—) just as we saw in ethylene. If

hydrogen gas under pressure is stirred up with the unsaturated fat in the presence of powdered nickel as a catalyst we find that the unsaturation disappears and the liquid fat becomes solid. We may write the chemical reaction for this change.

The reaction is permitted to take place until enough stearin is present to give the resulting fat the correct consistency or body. The powdered nickel is filtered out and the fat sold as "Crisco," "Spry," and "Snowdrift."

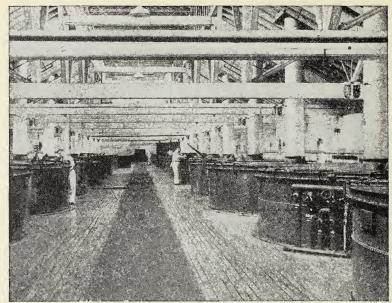
Paints. Linseed oil, which is obtained from flax seed, contains a large proportion of a glycerin ester of another acid which is still more unsaturated. The acid is *linolenic acid* and it contains three sets of double bonds between carbons in each molecule. The formula for this ester is:

Because of the amount of unsaturation which is present this substance is quite reactive. It reacts with the air to form a resinous material which will finally harden to a tough mass. If spread out as a film on a surface this oil reacts with oxygen much faster and forms a tough protective coating. In use the oil is mixed with finely powdered solids, called pigments, and the resulting material is called paint.

In actual practice the manufacture of paint is not quite so simple. The pigments must be opaque solids ground to extremely fine powder. The covering power of the paint depends upon this. The preparation of these pigments is an industry in itself. One of the oldest pigments known is white lead which is basic lead carbonate. This may be considered as a molecular mixture of lead carbonate and lead hydroxide. Its formula is Pb(OH)₂·2 PbCO₃. Additional white pigments are: basic lead sulfate; zinc oxide; lithopone, which is an especially prepared mixture of zinc sulfide and barium sulfate; and titanox, which is titanium dioxide. The finely pulverized solids are ground in oil and then mixed with additional oil and thinner to make the finished paint. The hardness of the finish, its lasting qualities, and the ease of repainting are largely dependent upon the pigment used.

If pure linseed oil is used with a pigment to make paint the resulting product requires considerable time to dry. It does not always have the correct body and it may be inclined to run or flow after being applied to a wall. To correct this difficulty the oil is treated. Some of the oil may be "blown." In this process the oil is heated and air is blown through it in order to raise its viscosity and give it body. To speed up drying it is customary to include a certain amount of "boiled" oil in the paint. This term is misleading since the oil so called has not really been boiled. It has been heated with a small amount of the oxides of lead and manganese. These serve as catalysts and cause the resulting product to react with oxygen much faster.

Linseed oil is not the only oil used in the manufacture of paint and it is not always the best to use under certain conditions. It is, however, the most widely used in paint for the exterior of buildings. One of the chief competitors of this oil is tung oil which is usually referred to as chinawood oil. Tung oil is composed of various unsaturated oils and when properly treated is a superior oil for paints and varnish. It is more resistant to water than linseed oil and it dries much faster. In order to give the paint film added pliability it is customary to include a small amount of an oil such as soy bean oil which does not dry so hard as the usual paint oils. It then acts as an internal lubricant.



Courtesy of The Procter and Gamble Company

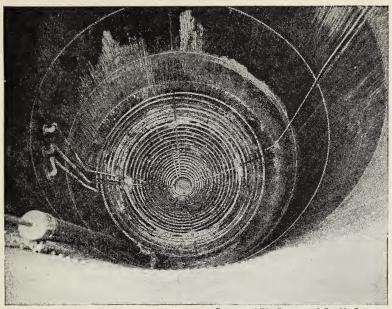
Fig. 99. The Kettle Room

Each kettle is three stories deep and will hold almost 300,000 pounds of soap - 10 carloads.

Varnish. As ordinarily used the term varnish is applied to solutions of various resins in solvents and thinners. These resins may be naturally occurring ones such as shellac, rosin, and copal, or they may be synthetic material. If the resins are dissolved in linseed oil or tung oil the varnish dries by reaction with oxygen. Such drying must be speeded up with "driers" which are the salts and oxides of lead, cobalt, and manganese. If the varnish dries by the evaporation of the solvent or thinner it is called a spirit varnish. Shellac is such a varnish.

SOAP

All of the natural fats will react with sodium hydroxide or other alkaline materials (saponification) to give a salt of the "fatty" acid together with glycerin.



Courtesy of The Procter and Gamble Company

Fig. 100. Look into an Empty Kettle.

The steam pipes three stories below are perforated and serve to heat the mixture of alkali and oil when the kettle is full.

$$(C_{17}H_{35}C O -)_3C_3H_5 + 3NaOH \rightarrow$$
Stearin
$$3C_{17}H_{35}C O - Na + C_3H_5(OH)_3$$
sodium stearate
(soap)

It just happens that the sodium (and potassium) salts of these long chain acids act in such a way that we can use them for soap. The glycerin is separated from the soap by the addition of salt to the hot water solution of the mixture. The soap is insoluble in hot salt water and floats to the surface where it is removed to molds for cooling. The water is evaporated and the glycerin and salt recovered. The largest supplies of glycerin come from the manufacture of soap, but it can be produced from other sources.

It has been pointed out that the solid or liquid nature of a fat depends upon whether or not the molecules are saturated. In much the same way we can say that the firmness of a soap depends upon the same thing. If a soap is made up entirely of sodium stearate it is so firm and has such a high melting point



Courtesy of The Procter and Gamble Company

Fig. 101. Blowing Bubbles

Liquid soap is sprayed into the top of this tower with steam pressure. As the small bubbles descend they are dried to form beads or granules. that extremely hot water must be used in order to produce a lather. Such a soap is satisfactory for laundry machine use but is wasted if used for hand dishwashing or toilet. If the soap contains some sodium oleate its melting point is considerably lower and it lathers well in moderately warm water. All of this may be controlled by using the correct mixture of fats in the soap manufacture.

A considerable amount of soap is made entirely from vegetable oils. In many instances these oils are first treated with hydrogen as in the manufac-

ture of cooking fat. This treatment increases the percentage of saturated compounds in the oil and, by this means, brings about the formation of the correct mixture for the soap wanted. The making of good soap has grown into a complex business and in the United States has achieved considerable proportions. Some idea of the enormous size of the industry may be obtained from the fact that in a normal year the production of soap and soap products exceeds 2,000,000,000 pounds in this country alone. This soap is produced from tallow, garbage grease, coconut oil, olive oil, palm oil, fish oil, cottonseed oil, corn oil, and soy bean oil. The use to which

the soap is to be put determines, to some extent, the type and source of fat used in its manufacture.

Soap and Hard Water. It was pointed out earlier that hardness of water is due to calcium and magnesium compounds which may be present. With soap these compounds form insoluble substances which appear as a scum on the water and the ring on the washbowl or bathtub. We may write the reaction for their formation.

$$2C_{17}H_{35}C \overset{\bigcirc{O}}{\longrightarrow} O - Na \ + \ CaCl_2 \xrightarrow{} (C_{17}H_{35}C \overset{\bigcirc{O}}{\longrightarrow} O)_2Ca \ + \ 2NaCl \\ \text{calcium stearate} \\ \text{(insoluble)}$$

Until all of the calcium and magnesium salts have been used up it is impossible to produce a lather in hard water. It follows from this that considerable soap must be wasted wherever hard water is used. Many softening agents are used to prevent this loss of soap.

Soapless Soaps. Within recent years a new type of cleansing agent has appeared. The esters which are present in fats may be treated with hydrogen in the presence of a catalyst made from the oxides of copper and chromium. Under such conditions these long chain acids are changed to the corresponding alcohols. This has been applied particularly to a fat which is prepared from coconut oil.

$$\begin{array}{c} H \\ \downarrow \\ C_{11}H_{23}C \stackrel{\frown}{\longrightarrow} O - C_2H_5 \ + \ 2H_2 \rightarrow C_{11}H_{23}C - OH \ + \ C_2H_5OH \\ \text{ethyl laurate} \\ H \\ \text{lauryl alcohol} \end{array}$$

The resulting alcohol will react with sulfuric acid to form a sulfonated product.

$$\begin{array}{cccc} C_{11}H_{23}CH_2OH \ + \ H_2SO_4 \longrightarrow C_{11}H_{23}CH_2OSO_3H \ + \ H_2O \\ lauryl \ alcohol & lauryl \ sulfonic \ acid \end{array}$$

With caustic soda or sodium carbonate this last product forms the sodium salt (C₁₁H₂₃CH₂OSO₃Na) which has remarkable properties when used in place of soap. It causes water to lather

and hard water does not affect it in any way. Thus it will lather just as well in hard water as in soft water. This is due to the fact that its calcium and magnesium salts are soluble in water. There are several such sulfonated compounds used and they are sold under trade names such as "dreft" and "gardinol." These products cost more than soap but are cheaper to use in hard water.

Fats as Foods. Fats and oils are essential food materials. They serve as fuel to keep the body warm and to supply energy. Also they serve as material for building fatty tissue within the body. It is very necessary to realize, however, that fats cannot be utilized by the body until they pass through the walls of the digestive organs. These digestive organs are the stomach and the intestines, the walls of which are like any other animal membranes. They are like very fine sieves or filters. It is possible for small molecules in water solution to pass through them but larger molecules are held back. Now the molecules of fat are large and since there are three large acid radicals hanging on to one glycerin radical it is almost like the branches of a small tree. Any one of the branches alone may pass through the walls of the intestines but taken all together it would be like trying to put a small tree through the openings of a tennis net. The body has solved this problem in a most wonderful way. The branches are cut off from the molecule and each part passes through separately. Once through the walls of the digestive organs the branches recombine and form the fat again unless they are first burned as fuel.

This process may be described chemically. We have seen how fats may be split into glycerin and fatty acids by means of alkali. This process is called *saponification*. The body carries on just such a saponification but is able to do it remarkably well. Now the contents of the stomach are acid because dilute hydrochloric acid is delivered to the stomach by certain glands. Because of this it is impossible for the fats to be saponified in the stomach. Near the first part of the small intestine there are two small openings. One of these forms a connection with the gall bladder which empties an alkaline solution called the bile into the small intestine whenever a fat is present. This alkali may start the saponification of the fat but, more important still, it causes the fat to break up into small droplets. These are suspended very much like colloidal particles in the fluid of the intestine. The other opening into the intestine forms a connection with the gland known as the pancreas. From this gland there is emptied into the intestine a fluid known as the pancreatic juice. Within this juice there are several substances which act as catalysts (enzymes) for digestive processes. It, too, is alkaline.

From the standpoint of the digestion of fats we shall mention one of these catalysts called *steapsin*, which actually means "to digest stearin." This enzyme comes into contact with the small droplets of fat and causes the molecules to split

into the acid and glycerin.

Each of these substances may then pass through the walls of the intestine into the blood stream where it is properly cared for. All of the fat so digested which is not used as fuel is recombined to form fat and then stored in the fatty tissues within the body.

SYNTHETIC RESINS

The natural resins such as rosin and shellac are esters of fatty acids with alcohols other than glycerin. They occur as products from the sap of trees or from insects. These have long been known and used in varnish manufacture. Synthetic resins are now displacing them from many of their former fields of usefulness and are, in many cases, superior to the natural products. Because of this similarity of usefulness it may be well to consider the entire field of synthetic resins at this time.

Bakelite. As early as 1872, Baeyer, a German chemist, discovered that phenol (carbolic acid) would react with various

aldehydes in the presence of acids, or bases, or ammonia, to give a sticky mess. After this, a number of other investigators tried to use this reaction in the preparation of a useful commercial resin. All of them failed until an American chemist, Bakeland, in 1909 found how to do it.

In general, the process involves heating formaldehyde with phenol until a reaction takes place. The relative amounts of the two reactants determine the hardness of the finished product. The amount of catalyst, and whether it is an acid, base, or ammonia determines the properties of the resin. The rate as well as the length of heating has much to do with the process also. The conditions are worked out and controlled exactly so that the same equipment may turn out a transparent plastic material or an opaque hard product.

The chemistry involved brings in little that is new. The large molecules necessary for the resin are formed from the union of a number of smaller molecules.

The first product upon prolonged heating may polymerize by splitting out water.

It will be noticed that this substance still has an arrangement of its atoms similar to that in the first product. It can react with yet other molecules and finally yield molecules of enormous size.

The amount of formaldehyde used may be increased.

This new material has two points in each molecule where further reaction may take place and upon further heating we will get molecules with chains going in two directions with cross links between them. These may be compared with the structure of wire netting. A resin made under these conditions is hard and firm.

By careful control of the amounts of reactants together with the heating time it is possible to get a product which is soluble in certain solvents. The resulting solution may be called a varnish. After application to a metal surface it may be heated and thus caused to form larger molecules which are no longer soluble in ordinary solvents. Heating is said to "cure" the resin.

Instead of making a resin which is soluble in solvents the process may be changed to give a solid which can be ground

to a powder or cast into rods. Upon heating, these become soft and may be molded to any desired shape. The heating also brings about further chemical union with the formation of large molecules and a resulting increase in hardness and elevation of melting point. In fact, the material, after this heat treatment, will char without any signs of melting. In order to obtain a compact product this molding is done at high pressures of 2,000 pounds or more and at 150° to 200° C. To improve the working qualities of the material to be molded it is general practice to mix wood flour or other fine fibrous material with the resin. This also improves the strength of the finished product.

Resins prepared as just described are used in molding automobile parts, telephone equipment, handles of various kinds, and electrical insulators.

Alkyd Resins. Within the past ten years we have seen the production of resins in ever-increasing amounts. These fall into general classes of similar materials and we shall not attempt to identify them as particular substances. Way back in 1847 a Swedish chemist, by the name of Berzelius, discovered that tartaric acid and glycerin would react together to give a resin. In those days when a chemical reaction produced a resin you did not try to find a use for it; you threw it away and, if possible, kept from getting it again. Now tartaric acid molecules have two acid groups. When these react with glycerin an ester is formed.

You will notice that the glyceryl tartrate still has one hydroxyl group which can react with half of another molecule of acid. The other half will have to find another molecule of glycerin somewhere. When these molecules get all mixed up they cannot tell what they are reacting with and before we know it they have formed some large molecules. This should produce a resin.

The resin so produced is formed from an alcohol and an acid. In order to name these resins someone took "al" from "alcohol" and "cid" from "acid" and combined them. For the purpose of pronunciation this has been changed to "alkyd" and this name has stuck. They are now called the alkyd resins.

The resins formed from tartaric acid were not very good. Later it was discovered that *phthalic anhydride* would behave like tartaric acid and do better. With glycerin this reacts to produce an ester.

 \mathbf{H}

 \mathbf{H}

The phthalic anhydride reacts with only a part of the glycerin molecule just as tartaric acid did. Further reaction causes the formation of large molecules to give a resin. If the reaction is permitted to continue it finally produces a completely hard substance. By including a small amount of an acid having just one acid group to the molecule, or a small amount of an alcohol with only one hydroxyl group to the molecule, the acid and alcohol will come out even once in a while and thus limit the size of the molecules. Hence it is possible to get various stages of hardness. This makes these resins quite adaptable.

If you will recall, in the discussion of solutions we said that "like dissolves like." These alkyd resins are esters. Rosins and other natural resins are esters. Linseed oil and tung oil are esters also. Here we have a natural set up for the inclusion of alkyd resins in paints and varnishes of all descriptions. They will mix in a satisfactory manner with almost anything which goes into a surface coating. By including certain nondrying acids within their make-up it is possible to have the *plasticizer* or internal lubricant as a part of the molecules. This prevents their loss through evaporation. It is small wonder that these resins are used in the finishes for fine automobiles and the best of furniture.

Other Resins. The preceding discussion gives some idea of the essential principles of resin formation. To discuss all of the types of resins at such length would occupy much space and include little that is new. Some of these are listed with the essential reaction of their formation.

Acrylic resins are formed from esters of acrylic acid. A widely used substance is the methyl ester.

$$CH_2 = CH - C OCH_3$$

This substance is unsaturated and exceedingly reactive. Under the influence of light, heat, and oxygen it polymerizes to form long chains. Such large molecules as result are resins.

These particular resins are entirely colorless and as clear as the finest glass. They are cast into sheets and used in place of glass in airplanes. Because of their crystal clearness they may be used for spectacle and other lenses which may be molded. Along the roadside we see reflectors which are made of this material. Since these resins may be colored with pigments they are finding use in making dentures and the exact color of the mouth may be duplicated. Rods of these resins possess the unique property of bending light. Light entering at one end of a rod will follow the rod in spite of bends. A popular name for this material is "lucite."

Styrene resins are produced by the polymerization of styrene.

This forms long chain molecules which are colorless and extremely clear. Such resins may be colored to any desired shade and molded exactly to any shape. They resist chemical action and films of thinnest dimensions have unusual insulation properties. A common name is "styron."

Vinyl resins are, in general, produced from derivatives of vinyl alcohol.

$$CH_2 = CH - OH$$

Usually the acetic acid, or the butyric acid, esters are caused to polymerize in the presence of a catalyst. The unsaturated molecules react together to form long chain molecules. After this some of the acid radicals may be saponified off by means of alkalies or other changes may be brought about, but the essential characteristics of these resins remain unchanged. A great use of resins of this type is in the middle of shatter-proof glass where it binds the glass and prevents

flying splinters in case the glass is broken. A well-known name among such resins is "vinylite."

Urea resins are interesting, indeed, since they are made from the four gases: ammonia, carbon dioxide, hydrogen, and carbon monoxide. Ammonia and carbon dioxide are used to produce *urea*.

$$O = C$$
 NH_2
 NH_2

Carbon monoxide and hydrogen react to form methyl alcohol from which formaldehyde may be produced. Urea and formaldehyde react by forming large molecules.

$$O = C \begin{tabular}{c|c} & H & H \\ \hline & H \\ \hline & H \\ \hline & V \\ \hline & H \\$$

Under the influence of heat and acids these molecules which are first produced react with each other to give a hard and inert product. By controlling the reaction the products may be used for "crush-proofing" fabrics, heat-setting adhesives, tableware, and enamels which are baked on. These products are known as "beetle" or "plaskon."

Cellulose resins include those substances which are made by treating cellulose with nitric and sulfuric acids (nitrocellulose), or with acetic anhydride and acetic acid (cellulose acetate). These products find use in the general plastic field but the discussion of their formation will be given under the chemistry of cellulose.

Future of Resins. The general field of resins has another

name which is just as appropriate. All of these things are classed as *plastics*. The public seems to like the latter name and so we hear much of the plastics industry. The present trends are for everincreasing expansion among all of the manufacturers. The materials are constantly improving and the prices are going down each year. Methods of fabrication of finished products are gradually being improved and the number of articles and uses are increasing. There can be no doubt as to the place of plastics in our everyday living. They fill a need and are here to stay.

SUMMARY

Fats are esters of glycerin with fatty acids. Those with long chain saturated acids are solids or semisolids and similar ones with unsaturated acids are liquids. The liquids may be converted into solids by hydrogenation.

Paints contain pigments suspended in an unsaturated oil such as linseed oil. This oil will react with the oxygen of the air to form a tough film. The reaction with oxygen is hastened by the addition of driers and the paint is made more fluid by the addition of thinners.

Varnish is made up of resins dissolved in drying oils such as linseed oil and tung oil, or in solvents such as alcohols and turpentine. The first of these dries by oxidation while the latter dries by evaporation of the solvent. Varnish which contains a pigment is called an enamel.

Soap is made by treating an animal or vegetable oil or fat with alkali. The sodium and potassium salts of long chain fatty acids are soaps. Glycerin is a by-product of soap manufacture.

Soapless soaps are the sodium salts of sulfonic acids made from alcohols with twelve or more carbon atoms in their molecules. These salts are not affected by hard water though their cost is greater than that of soap.

Fats are digested by a process of saponification brought about by enzymes. The acid and glycerin pass through the walls of the digestive tract and recombine to form fat.

Synthetic resins are taking the place of natural resins and

finding new uses for themselves. All of these are formed by processes whereby a number of small molecules combine to form large molecules. Under the influence of heat many of these form still larger molecules which are solids at all temperatures up to their burning point.

REVIEW QUESTIONS

- 1. What is the difference between a plant oil and petroleum?
- 2. To what class of organic compounds do fats belong?
- 3. What is the difference between animal fats and vegetable oils?
- 4. How may a vegetable oil such as cottonseed oil be converted to a fat?
- 5. What property makes possible the use of linseed oil in paint?
 - 6. Why do some paints contain an oil such as soy bean oil?
- 7. Name, and identify chemically, some of the white pigments.
 - 8. Explain the difference between raw and boiled linseed oil.
 - 9. In what respect does a varnish differ from a paint?
 - 10. Describe the manufacture of soap. What is the by-product?
- 11. For general household use most persons prefer a powdered or a flaked soap. Would the source or kind of fat used in its manufacture make any difference?
- 12. What causes the curd which one gets with soap in hard water? How prevent it?
- 13. What do we mean by soapless soaps? What is their advantage?
- 14. Trace the digestion of a fat in the body. How is this like soap making?
- 15. To what extent are the synthetic resins formed by processes which are alike?
- 16. Why do most synthetic resins set to permanent solids upon prolonged heating?
 - 17. Why are the alkyd resins so much used in surface coatings?
- 18. Would you class the manufacture of synthetic rubber with that of resins? Why?

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CARBOHYDRATES. PROTEINS. DIGESTION

CARBOHYDRATES

The process which we call photosynthesis is really a marvelous thing. We have considered the fats which, in plants, are formed by this photosynthetic process using carbon dioxide and water as the raw materials. These substances are, for the most part, made up of carbon and hydrogen with only a little oxygen. They are almost completely insoluble in water but are soluble in petroleum hydrocarbons. Now we come to another group of substances formed by photosynthesis. These, too, contain carbon and hydrogen, but the percentage of oxygen is much greater than in the fats. They are known as the carbohydrates. Those which are soluble will go into solution in water but are insoluble in petroleum. This fact alone indicates a considerable difference between the fats and these carbohydrates.

The common representatives of the carbohydrates are the sugars (there are many sugars), starch, and cellulose. During the early days of chemistry as a science all of these which were known were analyzed. They were found to contain carbon, hydrogen, and oxygen. For some strange reason the hydrogen and oxygen are present in the proper proportions to form water. When strongly heated, these substances decomposed with the formation of free carbon and the evolution of steam. There were some other things which came off, too, but they made little impression on the workers. Someone suggested that these substances were compounds of carbon and water, much like the water-containing crystals which we call hydrates. Thus the name *carbohydrate*. We now know that these are not hydrates of carbon at all but the original name sounds well, and

no one has thought of a better one, so they are still carbohy-drates.

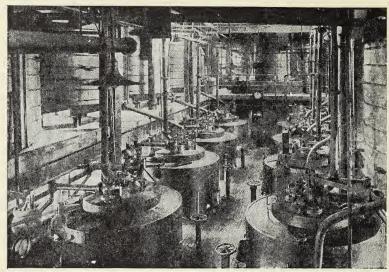
The Sugars. The name of sugar has been applied to a certain group of carbohydrates which have a sweet taste. In so far as we are concerned, there are two important classes of sugars, monosaccharides and disaccharides. Monosaccharides have the general formula $C_6H_{12}O_6$ and cannot be broken down into more simple sugars. For this reason they are called the simple sugars. The disaccharides have the general formula $C_{12}H_{22}O_{11}$. By their reaction with water these may usually be converted to more simple sugars with the formula $C_6H_{12}O_6$. The common monosaccharides are dextrose (glucose or grape sugar) and levulose (fructose or fruit sugar). The common disaccharides are sucrose (cane, beet, or maple sugar), maltose (malt sugar), and lactose (milk sugar).

Dextrose and Levulose. When we discussed photosynthesis it was suggested that formaldehyde was formed from water and carbon dioxide. This substance polymerizes to form the simple sugars.

$$\begin{array}{ccc} 6CH_2O & \longrightarrow C_6H_{12}O_6 \\ formaldehyde & monosaccharide \end{array}$$

The chemical structure of dextrose shows it to be an alcohol "five times over" and an aldehyde also.

The broken lines are supplied to indicate these two kinds of groups within the molecule. There is an isomer of glucose which is called *levulose*.



Courtesy of the Corn Products Refining Company

Fig. 102. Converters

Each of these converters, made of bronze to resist chemical action, holds 2,200 gallons. In them the starch is converted to dextrose by the use of water containing hydrochloric acid which is heated under pressure.

In certain plants such as the sugar cane and sugar beet it appears that a molecule of dextrose reacts with a molecule of levulose to form a molecule of sucrose and water.

$$C_6H_{12}O_6 + C_6H_{12}O_6 \rightarrow C_{12}H_{22}O_{11} + H_2O$$

dextrose levulose sucrose

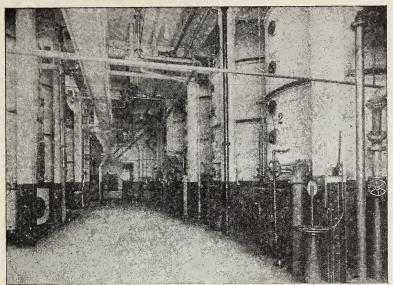
This is not unusual to expect since both dextrose and levulose contain reactive groups within their molecules.

Dextrose, or glucose, occurs in the juice of many ripe fruits, in molasses, and in honey. The blood stream normally contains about 0.1 percent of glucose resulting from the digestion of carbohydrate foods. Glucose is utilized directly by the body as a fuel. It represents the final stage of carbohydrate digestion.

If cane sugar is treated with water in the presence of a little acid it forms dextrose and levulose.

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

sucrose dextrose levulose



Courtesy of the Corn Products Refining Company

Fig. 103. Vacuum Evaporators

The clear filtered syrup from the converters is evaporated in these special vacuum pans to give "Karo" and other similar syrups for candy making, baking, and preserving and canning of fruits.

This same change is brought about by the action of an enzyme (*invertase*) which occurs in yeast. Within the body there is another enzyme (*sucrase*) which brings about the same change. This mixture of dextrose and levulose is called *invert sugar*.

Most of our commercial glucose is made by the hydrolysis (reaction with water) of starch. Corn starch is used in the United States while potato starch is used in Europe. The starch in water is heated under pressure with a small amount of dilute hydrochloric acid. After about two hours most of the starch has been changed to glucose.

$$\begin{array}{c} (C_6H_{10}O_5)_x \,+\, XH_2O \longrightarrow XC_6H_{12}O_6 \\ \text{starch} \end{array}$$

The acid in the resulting solution is neutralized with sodium hydroxide and the little bit of salt formed is left in the liquid. The sweet liquid which results is evaporated to a thick syrup

Courtesy of the Corn Products Refining Company

Fig. 104. Centrifugals

In these round, whirling basket sieves the glucose is separated from any uncrystallized syrup.

and sold to sweeten candy and other confections. Frequently the syrup is concentrated to the point of crystallization by evaporation in pans placed in ovens where the air pressure is kept low. By this means the water is evaporated at about 50° C. so that the glucose does not decompose and char. The solidified glucose is separated from the concentrated solution and freed from extra syrup by whirling in rapidly rotating sieves (centrifuge). The product from this operation is snow-white and is sold as dextrose. One common product is sold as "cerelose." This manufacture of syrup and dextrose uses up a billion pounds of corn each year.

Levulose occurs in many fruits and in honey. A substance, *inulin*, which is much like starch and occurs in the Jerusalem artichoke and in dahlia bulbs, will yield levulose when subjected to hydrolysis. It is formed from cane sugar, too, by hydrolysis.

Cane Sugar. Cane sugar or sucrose belongs to the class of substances known as disaccharides. It is identical in every way with the substance known as beet sugar. It occurs in the sugar from maple sap and in the juice of many plants, particularly the sugar cane and the sugar beet. In its preparation from cane the stalks are squeezed through heavy rollers to get the juice which may contain about 14 percent of sucrose. The acid nature of the juice is neutralized with lime which causes most of the unwanted material to settle out. The resulting clear juice is filtered and evaporated under low pressure. Crystals form and these are freed from syrup by whirling in a basket sieve. The solid so obtained is crude sugar and is sold to the refineries. It contains about 95 percent sucrose, 1 percent glucose, some mineral salts, and moisture. It has considerable brown color and a slight odor.

The preparation of the crude sugar takes place near the fields where it is grown. This means that most of our crude cane sugar is imported from Cuba and other tropical islands. A considerable amount is grown and prepared in Louisiana. The raw or crude sugar is sent to the refineries where it is

bought on the basis of sucrose content.

The main job of the sugar refinery is to remove the color and odor from the raw sugar. The refineries, therefore, first mix the raw sugar with the solution from which they have previously crystallized a batch of pure sugar. This removes most of the color but, since it is saturated with sugar, does not dissolve the crystals. The washed crystals are dissolved in the smallest amount of hot water in which they may go into solution, and the hot solution is filtered through beds of activated charcoal. This absorbs all of the color and odor which may be present. The filtered solution is evaporated under greatly reduced pressure and crystals are obtained. The process is most carefully controlled and the product is one of the purest substances on the market. It is remarkable that a pure compound can be produced and sold retail at five cents per pound (only baking soda rivals it in purity and price).

Beet Sugar. The sugar beet is a great source of the com-

Lienant

pound, sucrose. Central Europe has been a principal producer for many years. In the United States the beet production is greatest in the middle west. The first beets used had a sugar content of about 8 percent but by selection of seeds from high sugar plants it has been possible to increase the sugar content of them to about 16 percent. Some run as high as 18 percent.

To get the sugar from the beets they are sliced into thin slices. These are placed in tanks where hot water is run at the proper rate to give maximum extraction of the sugar. The resulting sweet solution contains about 12 to 15 percent sugar. This is treated with lime to neutralize acids and to precipitate unwanted material. The excess lime is then removed by passing in carbon dioxide. After filtration, the solution is evaporated in low-pressure pans and the crystals which form are whirled in centrifugals as previously described. The white crystals which result are identical in every way with cane sugar. Any apparent difference in crystal size is due to rate of crystallization.

Maltose. When starch is acted upon by an enzyme called diastase it is converted into a sugar called maltose ($C_{12}H_{22}O_{11}$). This process occurs during the sprouting of grain. Maltose is an isomer of sucrose. During digestion in the body maltose is converted to glucose by the action of an enzyme.

Lactose. Milk is the only natural source of lactose or milk sugar. It, too, is an isomer of sucrose with the formula $C_{12}H_{22}O_{11}$. The milk from cows contains about 5 percent of lactose. When milk sours it is due to the conversion of the lactose into lactic acid.

$$\begin{array}{c} \text{OH} \\ \text{O} \\ \text{I} \\ \text{C}_{12}\text{H}_{22}\text{O}_{11} \ + \ \text{H}_2\text{O} \rightarrow 4\text{CH}_3\text{--C}\text{--C}\text{--OH} \\ \text{Iactose} \\ \text{H} \\ \text{lactic acid} \end{array}$$

This change is brought about by the action of bacteria which are present in the air. It is interesting that yeast does not bring about the fermentation of lactose.

Comparative Sweetness. The question of how sweet is a sugar is largely a matter of debate. It must rest with people to state their reaction to the taste of a substance. Under the best of controlled conditions it is possible to make out a scale of sweetness which is approximately correct. On this basis the sweetness of sucrose is taken as 100. Levulose has a rating of 173, dextrose is 74, maltose is 32, and lactose is 16.

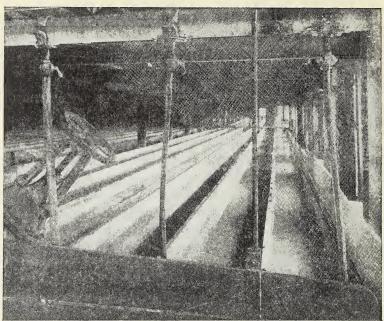
Starch. Plants store food in the form of starch. Usually this is deposited within the seed or surrounding the seed so that the young plant may be properly nourished until its roots begin to function. It seems that all starch, from whatever source, is the same chemical substance but it does not look the same. Starch appears in small granules. Under the microscope these granules are quite different in starch from different sources. A trained worker is able to tell the source of the starch at once by observing these granules.

Preparation of Starch. Almost all of the starch produced in this country is prepared from corn. The kernel of corn has an exterior covering called the hull which is principally fiber. The main portion of the kernel is a mixture of starch and gluten. At the point of the grain there is the embryo or germ which contains oil, gluten, and fiber. The various substances which are present may be classed as soluble, germ, hull, starch, and gluten.

The initial step is the removal of soluble material with warm water which is saturated with sulfur dioxide. The sulfur dioxide forms sulfurous acid with the water and serves to prevent fermentation or spoiling. The resulting solution of soluble material is evaporated to a syrup and added to cattle feed.

The corn which has become softened by some forty hours' soaking is ground in a special mill which tears the kernel apart without injury to the germ. The germ with its oil is lighter than the rest of the material and is floated off by means of water. Simple filtration through a sieve serves to separate this germ from any small starch grains. The germ is then crushed and pressed to obtain the oil.

The germ-free material is ground to separate the starch and



Courtesy of the Corn Products Refining Company

Fig. 105. Starch Tables

The mixture of starch and gluten (corn protein) is suspended in water and run over these trough-like tables where the starch settles out in deep layers.

gluten from the hulls. It is then sieved to remove the coarser fiber material and passed over shakers where the starch and gluten, together with water, pass through a fine-mesh silk screen. Any fiber present is coarser than the starch and remains behind. The fiber is dried and used for feed. The mixture of starch and gluten is passed onto long tables where the heavier starch settles out as the solution slowly makes its way. On this table the starch forms a firm cake. This cake is again stirred with water and filtered to remove any impurities which may be washed out. The snow-white product is then ready for the preparation of dry starch products or the preparation of the various syrups and dextrose.

The gluten which has been separated is filtered from the water and is used to prepare gluten feeds.

Chemistry of Starch. Starch is insoluble in water and in all other solvents. But if it is heated with water the granules burst and the grains of starch are scattered through the liquid. These grains are so very small that they show no tendency to settle out. Hence the so-called starch solution is really a colloidal suspension of starch grains, though it may be true that the actual starch grains are very little larger than the starch molecules. The starch which is present in a colloidal suspension presents a very large surface and because of this it is rapidly changed by chemical substances with which it may react. Various organic catalysts (enzymes) are able to bring about the change of starch to glucose quite rapidly in the presence of water.

The formula for starch is $(C_6H_{10}O_5)_x$. This implies that the molecule is some multiple of this formula. The molecules are large, we are sure, but just how large we cannot even guess. For instance the correct formula may be $C_{600}H_{1000}O_{500}$ or some such figure but we have no sure method of making this determination. All of our methods for getting molecular weights depend upon converting the substance into a gas or putting it into solution, and, since starch will not become a gas and is insoluble, there is nothing to be done about it as yet except to make estimates.

When starch is heated in the presence of water and a small amount of acid, it is first converted to *dextrin* which is a sweet substance related to starch. Some dextrin is formed on the surface of bread during toasting. There are actually several different kinds of dextrin. They differ in the size of their molecules though they, too, have the general formula $(C_6H_{10}O_5)_x$. The adhesive on stamps, envelope flaps and labels is largely dextrin. Further heating converts the dextrin to maltose which is a disaccharide. During the heating, the maltose is further changed to glucose. The production of glucose from starch has already been described.

During the sprouting of such grains as barley an enzyme called *diastase* is produced. This enzyme is able to cause the starch to change to maltose. If the sprouted grain is heated and

dried the product which contains diastase is called malt. When this malt is added to starch and water it causes the starch to be converted to a mixture of dextrin and maltose. This mixture is called *dextrimaltose* and is used as a food for children, in candy, and in malted milk drinks.

The Carbohydrates as Food. The carbohydrates such as starch and various sugars constitute a very important class of foods. These are easily changed to glucose within the body, and the glucose is absorbed by the blood. It is this glucose in the blood which is burned as fuel for heat and energy. Under normal conditions the blood contains about 0.1 percent glucose but this may vary. If carbohydrates are eaten there is soon a rise in the blood sugar. Some of this is used in muscular exercise, some is absorbed by the muscles, and some is changed in the liver and in the muscles to a more complex substance called glycogen which is commonly referred to as animal starch. This glycogen serves as a storehouse of carbohydrate in the body and may be drawn upon at any time if the blood sugar supply runs low.

Since glucose is a form of carbohydrate which the body can use without further digestion, it is common to find it used as a special food. In cases of starvation glucose solutions are injected directly into the blood stream in order to give the patient nourishment. Some people are unable to use glucose as a food and it builds up in their blood stream. The excess glucose in such persons is thrown off through the kidneys. This surplus of blood sugar has very harmful effects and it is essential that it be reduced or death will follow. The disease associated with this condition is called diabetes mellitus.

The normal body contains a catalyst called *insulin* which promotes the utilization of glucose. This catalyst is secreted by a portion of the pancreas and is discharged directly into the blood stream. The lack of this catalyst brings about the diabetic condition. Insulin is extracted from the pancreas of animals and is obtained as crystals. A solution of these crystals in carefully controlled amounts may be injected into the body and there it enables the diabetic body to use glucose. The use

of this substance has saved and prolonged many lives, and hence it must be placed among the great achievements of modern physiology.

The Digestion of Carbohydrates. Around each little granule of starch there is an envelope of cellulose which forms a thin skinlike covering. The human body is not capable of digesting cellulose and therefore raw starch is probably not used by the body at all. Hence the uselessness of eating raw potatoes and flour. But heat causes this cellulose covering to burst and permits the smaller grains of starch to be acted upon by the digestive system. As soon as cooked starch enters the mouth it becomes more or less mixed with saliva depending upon the amount of chewing which is done. Within the saliva there is an enzyme called ptyalin which serves as a catalyst for the conversion of starch to maltose. This change is by no means complete in the mouth. The action of the ptyalin stops soon after the food enters the stomach since the stomach juices are acid and there is no further change in the starch until it reaches the small intestine.

Such substances as cane sugar and milk sugar pass through the mouth unchanged. The acid in the stomach converts some of these into glucose and fructose but they mostly pass on to the intestine unchanged.

The pancreatic juice which has already been mentioned contains another enzyme called *amylopsin*. This enzyme is very much like ptyalin in that it catalyzes the conversion of starch to maltose but it is many times more powerful than ptyalin. Very little starch is acted upon before it gets to the small intestine but the amylopsin soon converts all of it to maltose.

From the walls of the small intestine there flows a juice which contains the additional enzymes *maltase*, *lactase*, and *sucrase*. Maltase serves as a catalyst for the conversion of maltose to glucose. Lactase catalyzes the split of lactose into glucose and another simple sugar called *galactose*. Sucrase brings about the conversion of sucrose into glucose and fructose.

From this discussion it may be seen that the entire process of digestion of carbohydrates is one in which large molecules are split up into smaller molecules which may pass through the intestinal walls into the blood stream. The effect of digestion of starch is the same as may be accomplished by heating the starch with water and acids.

$$Starch \rightarrow maltose \rightarrow glucose$$

Glucose represents the final stage of digestion of starch. The other simple sugars, fructose and galactose, which were mentioned may be used by the body as is glucose.

Cellulose. The fibers we know as cotton are really the flattened walls of hairlike cells which grow on the seed of the cotton plant. These, like the walls of many other plant cells, are composed of almost pure cellulose. The cells in trees have walls of cellulose and these are glued together, with a substance called *lignin*, into the firm structure of the tree.

The chemical formula for cellulose is very much like the formula for starch. It is written as $(C_6H_{10}O_5)_x$ but we do not know how large the molecule is. The subscript x must be very large because the cellulose molecule is too big to dissolve in any solvent. We assume that cellulose is made from many glucose molecules which have reacted together because we can make glucose from it. If we boil cellulose with water and an acid, the cellulose is slowly changed to glucose.

$$\begin{array}{c} (C_6H_{10}O_5)_x \; + \; XH_2O \longrightarrow XC_6H_{12}O_6 \\ \text{cellulose} \end{array}$$

This change goes so much more slowly than the change of starch to glucose that we are sure the cellulose molecule is much larger and possibly much more complex than the starch molecule.

There is no provision in the human body for the digestion of cellulose, but all animals that eat hay are able to use it for food. It is probable that their digestive tracts contain bacteria which are able to convert the cellulose to glucose. Quite a bit of attention has been given to the problem of making food material from waste wood and other cellulose. Methods have been devised whereby wood scraps may be heated with acids





Fig. 106. World's Largest "Sandwich Shop"

Thin polished plate glass, a triumph of modern chemistry and engineering, is used to make the high-test laminated safety glass which is standard equipment for windshields and windows of many makes of 1941 cars. In this huge "sandwich shop" of the Libbey-Owens-Ford laminating plant at East Toledo, Ohio, skilled workers cut the new plastic called "polyvinyl acetal resin" and then place it between panes of plate glass. Heat and hydrostatic pressure in an oil bath then are applied to weld the three parts into an integral pane of safety plate glass.

under pressure. The cellulose molecules are split and glucose is produced. After neutralizing the acid the glucose in water is used for stock food. At present this is not a commercial process but large-scale trial plants are operating. If such a process can be operated at a profit it will no doubt find use in some countries whose food supplies are limited.

Guncotton and Pyroxylin. Since it is possible to convert cellulose to glucose it seems probable that cellulose, too, may have alcohol groups within its molecules. Alcohols may react with acids to produce esters, and so it is with cellulose. With nitric acid cellulose reacts to form nitrocellulose (see Chapter 18) which is an ester of the alcohol groups in cellulose with

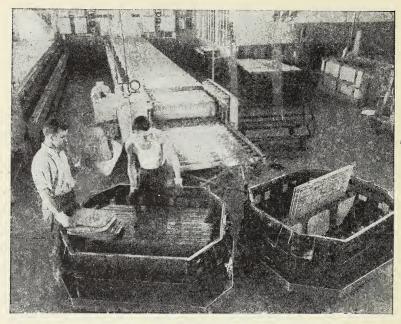


Fig. 107. Ready for Oil Pressure

This photograph shows high-test safety plate glass being placed in position for its hot oil pressure treatment. This process "welds" two thin panes of glass and the plastic filler into a crystal-clear unit to provide for safety and good vision during the life of the car. After it emerges from the oil bath the glass is ready to be washed and packed for shipment to automobile plants.

nitric acid. If all of the alcohol groups of the cellulose are so esterified (allowed to react with nitric acid) the product is an explosive called *guncotton*. This is used in the manufacture of smokeless powder for ammunition.

If the amount of nitric acid used with the cellulose is not sufficient to react with all of the alcohol groups in the cellulose molecule the product is called *pyroxylin*. This substance is soluble in a mixture of alcohol and ether while guncotton is not. This mixture is used to separate the two nitrocellulose products. The solution of pyroxylin is sold as "collodion" and as "Nu-skin" and is used with pigment for fingernail paints. Pyroxylin mixed with camphor and alcohol gives the product known as celluloid. Since celluloid may easily be colored with various pigments it lends itself to the production

of artificial ivory, tortoise shell, amber, and coral. The first "safety glass" was made by pressing a sheet of celluloid between two sheets of glass. When this is done the glass adheres to the celluloid and in case of breakage the glass splinters remain in place instead of flying. The glass so prepared had the bad property of turning yellow in use and now the celluloid is giving way to "vinylite" resins and to cellulose acetate.

Lacquers are produced by dissolving pyroxylin in a solvent such as amyl acetate, ethyl acetate, or butyl acetate. These solvents, it will be recalled, are esters of acetic acid with amyl, ethyl, and butyl alcohols. The pyroxylin solution so formed is mixed with natural or synthetic resins, plasticizers, and pigments. By the addition of thinners the resulting mixture may be brushed or sprayed onto the object to be coated. The solvent evaporates slowly leaving a coating of the nonvolatile material. If cloth is coated with such pyroxylin the finished

product is sometimes called artificial leather.

Artificial Silk. Throughout history silk has furnished the clothing for royalty, and the ordinary man has had to stand aside with envy in his heart. The alchemists tried in vain to make gold from lead, but we have no records of their ever making an attempt to produce the humanly more important silk from cotton, flax, or wool. Now silk is different from cellulose in many ways. In the first place it does not have the same chemical composition. Silk contains carbon, hydrogen, oxygen, and nitrogen and does not resemble cellulose in any manner. A French chemist, de Chardonnet, watched the silkworms eat mulberry leaves, and, without having any other food, spin a thread of silk. He thought that the chemist should be able to convert these same leaves to silk in the laboratory. He tried mulberry leaves and also various forms of cellulose. As a result of his investigations he used nitrocellulose dissolved in alcohol and ether. He pressed this through a small opening and the resulting thread was permitted to drop into a solution of calcium sulfide. The sulfide reacted with the nitrocellulose and removed most of the nitrogen. The thread which remained was almost pure cellulose and yet it was a continuous fiber and had the luster of silk. Some of this was exhibited at the Exposition of Paris in 1889.

Viscose. It is common experience in all scientific work that when one person gets an idea and lets it be known there are always others who are ready to jump in and carry it out in directions the originator never dreamed of. Within a short time chemists all over the world were thinking of artificial silk, too. The product made by de Chardonnet was not good. Other methods would have to be invented. It was soon realized that in order to get a long fiber of cellulose it would be necessary to tear apart the fibers as they grow in nature. This could be done by dissolving the cellulose but nothing would serve as the solvent. In 1892 two English chemists, Cross and Bevan, devised a method for making a compound of cellulose which could be dissolved and which could then be formed into a thread. The thread was treated with acid to destroy the compound and leave the pure cellulose as a glossy fiber. There were many trials before the method could be applied on a large scale, but now this method serves to prepare about 65 percent of all the "artificial silk" made.

Cellulose from wood or cotton is purified and treated with sodium hydroxide. Carbon disulfide (CS₂), a liquid prepared by heating carbon with sulfur in an electric furnace, is added and the cellulose forms a compound known as *cellulose xanthate*. This compound is thick and viscous and is known to the trade as "viscose." It dissolves in additional carbon disulfide and the solution so formed is forced through a set of very fine holes into a solution of sulfuric acid in water. This destroys the compound of cellulose and fibers of pure cellulose remain. The several fibers so made at once are twisted into a thread and wound on a spool. The thread has a luster which is like that of silk except that it sometimes outshines silk. This is known as the viscose process.

Uses of Viscose. There are many uses of viscose other than the manufacture of fibers. Quite a large amount of it is pressed through a narrow slit into acid to give the common transparent wrapping material known as "cellophane." For the millinery

trade viscose is used to produce artificial straw, and artificial horsehair. Wire netting coated with viscose is used as a substitute for window glass in poultry houses. This material permits the passage of a considerable amount of ultraviolet light which glass does not permit to pass. Other large uses are for the manufacture of sausage casings, bottle caps which fit close to the glass, picture film for cameras, and cellulose sponges.

Bemberg. Cellulose is soluble in a solution made by treating copper oxide with concentrated ammonia in water. This is called the cuprammonium process. This material may be forced into an acid solution as described above and the resulting filaments of cellulose spun into a thread. This thread is stronger than ordinary viscose and is useful in the manufacture of ladies hose. The product is known as "bemberg." It is noteworthy that the manufacture of this material was on the increase in 1939.

Celanese. Since the cellulose molecule contains alcohol groups, it occurred to some workers that it should react with acetic acid to form esters. To these esters they gave the name of cellulose acetate. Cellulose does react with acetic acid but reacts faster with a solution of acetic acid containing acetic anhydride. Acetic anhydride is made from acetic acid by taking water out from between two molecules of the acid.

$$\begin{array}{c} CH_3-C \stackrel{\bigcirc{}}{\smile} OH \\ CH_3-C \stackrel{\bigcirc{}}{\smile} OH \\ CH_3-C \stackrel{\bigcirc{}}{\smile} OH \\ \end{array} \xrightarrow[]{} \begin{array}{c} CH_3-C \stackrel{\bigcirc{}}{\smile} O \\ CH_3-C \stackrel{\bigcirc{}}{\smile} O \end{array} \xrightarrow[]{} \begin{array}{c} CH_3-C \stackrel{\bigcirc{}}{\smile} O \\ CH_3-C \stackrel{\bigcirc{}}{\smile} OH \\ \end{array}$$

acetic anhydride

The acetic acid and acetic anhydride mixture reacts with cellulose in a short time and forms a material which may be used in place of viscose. If fibers are made from this cellulose acetate it is not necessary to get back the pure cellulose. The fibers are dried by a stream of warm air. These fibers are in many ways superior to those made from viscose. Viscose fibers absorb water and lose more than half of their strength while wet. Cellulose acetate fibers absorb less water and they retain most of their strength while wet. Cloth woven from the acetate product has a high luster. It is sold as "celanese" and "acele."

The cellulose acetate fibers have given trouble about taking dyes. The cotton dyes would not color them and the wool dyes were not always satisfactory. This is partially cared for by treating the cellulose acetate with sodium hydroxide after the thread is formed. This removes the acetic acid radical from the ester and leaves pure cellulose on the outside of the fiber. Such cellulose will take the ordinary cotton dyes.

Another point which is frequently overlooked is the fact that acetate material is soluble in certain solvents which are frequently used for cleaning. It is slightly soluble in alcohol and is completely soluble in the liquids used to remove fingernail polish. They are safe in water with good soap, or in such solvents as pure benzol, gasoline, carbon tetrachloride, and turpentine. It is sometimes necessary to press clothing of acetate yarn. It must be remembered that cellulose acetate is melted by heat and should never be heated above 275° F.

Rayon. It is true that men tried at first to imitate silk, but that ambition no longer holds. The fibers which they have developed have found their own useful place alongside of silk and they are no longer trying to imitate anything. The proper methods of handling these fibers and the cloth made from them have been mastered and the clothing made from them has its own appeal. The entire field of artificial fibers has given the name "rayon" to its product in an attempt to emphasize the gloss of the material. The makers of acetate fibers have not taken to this name very well as may be seen from their continued use of "celanese" and "acele."

During 1939 the world production of rayon was more than 1,100,000,000 pounds. Of this the United States produced 330,000,000 pounds. It is probable that the United States is exceeded in this production by only one other nation, Japan, which we consider as the home of the silkworm.

Nylon. While we are on the general topic of man-made fibers it is well to mention one of the newer ventures in the field. About two years ago an American firm announced the

experimental production of a new fiber called "nylon." From the chemical viewpoint it resembles silk since they are both proteinlike nitrogen compounds. The basic chemicals for its production come from coal, air, and water. It is probable that its production may be classed as an outgrowth of the manufacture of "neoprene." Their search for artificial rubber led into other fertile fields. Fibers of nylon no larger than the web of a spider as well as bristles for toothbrushes may be made from it. Because of its great elasticity, strength, resistance to wear, and failure to absorb water it is reported to be an ideal material for hosiery and other knit goods. Already the commercial manufacture of garments of this fiber has started and they may be purchased at reasonable prices.

Mercerized Cotton. An earlier attempt to produce a glossy fiber from cotton resulted in the product which we know as "mercerized" cotton. When cotton is treated with concentrated sodium hydroxide it reacts to form what is known as oxycellulose. The fibers swell and become cylindrical like tiny rods. Under ordinary conditions the fibers will shrink when treated in this manner but by stretching them as they are washed and dried they retain their rodlike nature and take on a gloss. Much of the thread sold because it looks like silk is really mercerized cotton. It is stronger than untreated cotton and takes a dye much better. The man who devised the process of manufacture was named Mercer, and it was for him that the name was given to the product.

Paper. For all practical purposes we may define paper as a sheet of cellulose fibers which have been thoroughly mixed together while wet and pressed between hot cylinders until dry. The type of paper desired determines, to some extent, the source of the fiber, and, to a great extent, the treatment given the fiber during the process of paper manufacture. We have already discussed the use of chlorine gas to bleach cotton. Hence we would expect to use chlorine to bleach any other form of cellulose. All white paper has been bleached.

We are all acquainted with the properties of blotting paper

in which we are able to see the individual fibers. Even a casual

examination will show how thoroughly these fibers are enmeshed to form a mat. A drop of ink placed on such paper is quickly absorbed in much the same way as a sponge absorbs water, and naturally it will not do for writing purposes. If the fibers are coated with a waterproof material before the formation of the mat the ink will not be absorbed. By the use of clay, starch, and other "fillers" the open spaces between the fibers are filled so as to give a smooth writing surface.

Pulp. The fiber from which paper is made is called *pulp* and

Pulp. The fiber from which paper is made is called *pulp* and it may be obtained from any available source. Many years ago most of this pulp was obtained from old rags of cotton or linen, but with the present large consumption of paper there is not enough of such material to supply the demand. In addition to an actual shortage of rags the cost of collection would make the price too high. Paper made of cotton or linen, however, is of superior quality and will last much longer. Books which are designed for a lasting record as well as books which are to be much used are printed on rag paper. Some newspapers have a special rag paper edition intended for permanent files in libraries. The *New York Times*, for instance, will supply such an edition at a premium of about \$100 per year.

The greatest source of paper pulp is wood. The cellulose fibers of wood are glued together with *lignin* and the fibers must be torn apart and freed from this gumlike material in order to make pure pulp. For ordinary newsprint paper it is not necessary to remove all of the lignin since this paper is not prepared for a permanent record and need not be tough. This partial removal of the lignin is usually accomplished by mixing untreated pulp containing all of the lignin with pulp from

which all of the lignin has been removed.

In general there are two types of pulp produced from wood; mechanical pulp and chemical pulp. The mechanical pulp is produced by pressing the side of a log against a rapidly revolving grindstone. This tears the fibers apart. A stream of water flows over the stone and the fibers are fairly well suspended in the liquid while the larger pieces settle out or are screened out. Chemical pulp is made from wood chips by treating with

a solution of sodium hydroxide (*soda pulp*), or a solution of lime and sulfur dioxide (*sulfite pulp*). The soda process is applied to poplar wood and the sulfite process is applied to spruce. The differences in the two processes are due to the differences in the wood but the pulp in either case is the same. Both kinds of chemical pulp are bleached by adding lime together with chlorine gas.

Pulp from Southern Pine. Within the past few years considerable prominence has been given to a southern pine as a source of paper pulp. The tree in question is capable of growing to sufficient size to cut in about seven to ten years. The yield of pulp is quite high, and the tree may be grown as a farm crop. As would be expected, a special treatment must be given these fibers since these trees contain a high percentage of rosin and other gum material. As a rule this pulp is made by digesting the wood with a solution of sodium sulfate and sodium sulfide. The so-called *kraft* paper is made in this manner. It has been improved until now a satisfactory newsprint paper is being produced from this pine. With the present upset in economic affairs it is quite probable that many plants for the manufacture of this newsprint paper will be built in the southern part of the country. Another cash crop to take the place of "ex-king cotton" will certainly be of great benefit to that section.

Formation of Paper. The formation of the sheet of paper involves the same processes regardless of the type of paper desired. The actual treatment is, of course, different for different kinds of paper. Suppose we use the formation of newsprint paper as an example. A mixture of 1000 pounds of mechanical pulp together with 150 pounds of chemical pulp is put into a "beater" with a rosin compound and clay together with plenty of water. The mixture is called a "cream." The fibers are thoroughly separated and mixed with the rosin compound during this process. Aluminum sulfate (alum) is added to the cream and this causes the rosin to attach itself to the fibers. The cream is then diluted with large amounts of water and poured evenly onto an endless wire gauze which is the

width of the finished sheet. The water drains through the gauze, and the coated fibers together with the clay collect in the form of a mat on top of the gauze. The gauze is made to move away from the source of wet pulp at rates as high as 900 feet per minute. Cylinders, through which the gauze and the pulp which it carries must pass, squeeze out most of the water, and soon the wet sheet is dry enough to leave the gauze and pass alone between hot cylinders which finish the task of pressing and drying it.

Paper for books and other special purposes is made from chemical pulp alone and receives coatings of special materials along the path of the paper sheet. In every case these special coatings are for the purpose of giving a particular finish which

improves the paper for a particular use.

Other Uses for Pulp. The production of high-grade pulp from wood is an industry by itself. The purified and bleached pulp finds a use in the preparation of surgical dressings and other similar supplies. The manufacture of viscose, cellulose acetate, cellulose nitrate, and bemberg all start with such pulp as the source of cellulose.

PROTEINS

In addition to fats and carbohydrates a number of other substances, called *proteins*, are extremely important as foods. Within our bodies there are large amounts of these proteins present as muscle, bone, brain, and tendons. The fats and carbohydrates are essentially fuel foods and unite with the oxygen in the blood to produce heat and energy in much the same way as coal unites with oxygen of the air when it is burned in a furnace. The proteins, on the other hand, have a close relationship to the life processes and they make up the very seat of life in the living cells. As these cells die, which they do at varying rates, they must be replaced with other similar material and all new cells necessary for growth or maintenance must also be supplied from such substances. Even

plants contain proteins in order that their life processes may go on in the proper fashion. Eggs, milk, cheese, meat, beans, peas, and cereals are the usual sources of protein for our food.

Composition of Proteins. We have pointed out the complex nature of starch and related how it may be broken down first to dextrin, then to maltose, and finally to glucose. In many respects the proteins behave in a similar manner. The protein molecules are extremely complex and there is no way for us to know their actual size or weight. They are insoluble in all solvents and it is only through chemical action that they may be made to go into solution at all. They are broken down by the same chemical agents which bring about the decomposition of starch. Water containing a little acid will change the proteins into simple compounds in much the same way that starch is changed to glucose. All proteins do not yield the same simple substances when treated in this manner and a particular protein may yield several different compounds.

Unlike fats and starch the proteins contain the element nitrogen and this appears in each of the final simple compounds produced from the proteins. These simple compounds contain an acid group (—C^OOH) and an amine group (—NH₂) which is derived from ammonia. They are called amino acids and are frequently spoken of as the building blocks from which proteins are made. There are more than twenty different amino acids which have been obtained from proteins. The most simple amino acid is aminoacetic acid.

$$\begin{array}{c} H \\ | \\ C - C - OH \\ | \\ NH_2 \end{array}$$

It may be recalled that ammonia will react with acids to produce salts. In the same way the amino group may also react with the acid group to produce a substance which corresponds

to a salt. Thus two molecules of aminoacetic acid may react together:

It may readily be seen that the larger molecule formed still has an amino group on one end and an acid group on the other end. Each of these groups may again react. Now imagine twenty or more different amino acids which may react together in all possible combinations so that the products from the first combination may again react with themselves or with separate amino acids. Let this combination and recombination take place until hundreds of the smaller molecules are incorporated into the larger molecules and then you will have some idea of the complexity of the protein molecule.

The Digestion of Proteins. We must have proteins in our food in order that the body may have a source of repair material with which to rebuild worn-out tissue. The molecules of proteins are much too large to pass through the walls of the intestine and thus like starch they must be broken down into their simple components. The digestive process is able to convert proteins into simple amino acids which may pass into the blood stream. These amino acids are recombined within the body to produce the required proteins. Some proteins which we use for food do not contain all of the amino acids which the body requires and such foods are said to be incomplete proteins. Thus gelatin is not able to support life without the aid of some other protein. Milk contains all of the required amino acids and it is classed as a complete protein.

The digestion of protein material starts in the stomach in the presence of the dilute acid of the gastric juice. An enzyme, pepsin, is supplied in the gastric juice and acts as a catalyst for the decomposition of proteins into smaller molecules called proteoses and peptones. The acid is quite necessary for this decomposition and is said to activate the enzyme. The time which the food spends in the stomach is so short that not all of the protein is acted upon before being forced into the small intestine where the juices soon become alkaline through mixing with the bile. To care for complete digestion the pancreas secretes two enzymes, trypsin and erepsin, which bring about the complete change of all the protein into the simple amino acids. In order that no protein may escape unchanged, the walls of the intestines also supply large amounts of erepsin. The resulting amino acids pass into the blood stream and serve to build body cells.

Summary of Digestion. The processes of digestion have been described briefly in connection with the various food materials. The table which follows may be helpful as a summary.

Substance acted upon	Name of Enzyme	Found in	Change produced
Starch	Ptyalin Amylopsin	Saliva Pancreatic juice	$\begin{array}{c} Starch \rightarrow dextrin \rightarrow maltose \\ Starch \rightarrow dextrin \rightarrow maltose \end{array}$
Disaccharides	Maltase Sucrase Lactase	Intestine Intestine Intestine	Maltose \rightarrow glucose Sucrose \rightarrow glucose + fructose Lactose \rightarrow glucose + galactose
Fats	Steapsin	Pancreatic juice	Fats → fatty acids + glycerin
Proteins	Pepsin Trypsin Erepsin	Gastric juice Pancreatic juice Pancreatic juice and intestine	$ \begin{array}{l} \text{Proteins} \rightarrow \text{proteoses} + \text{peptones} \\ \text{Proteins} \rightarrow \text{proteoses} \\ \text{Peptones} \rightarrow \text{amino-acids} \\ \text{Peptones} \rightarrow \text{amino-acids} \\ \text{Peptones} \rightarrow \text{amino-acids} \end{array} $

SUMMARY

Such things as sugars, starch, and cellulose are classed as carbohydrates.

The common sugars such as dextrose and levulose are classed as monosaccharides while sucrose, maltose, and lactose are classed as disaccharides. The disaccharides may be split to monosaccharides by chemical action.

Dextrose is prepared by the hydrolysis of starch. Also, it is the final product in the digestion of starch.

Sucrose is prepared by crystallization of the purified and

evaporated juice from sugar cane and sugar beets.

Maltose is produced from starch by enzyme action. Lactose occurs in milk.

Starch is prepared from corn and is separated from the remainder of the kernel by grinding, filtering, and sedimentation. Starch is converted to maltose by enzyme action. The enzymes of the body bring about the conversion of starch and sugar to glucose and other simple sugars.

Cellulose forms the fibrous material of plants. It may be converted to dextrose by hydrolysis but the digestive system

cannot bring this about.

Cellulose will react with nitric acid to form cellulose nitrate and with acetic acid to form cellulose acetate. These are important plastics. Cellulose is used to prepare viscose for rayon and cellophane.

Wood fiber as well as cotton fiber and linen may be converted to pulp for paper and other cellulose uses. Wood pulp

is prepared either chemically or mechanically.

Paper is formed by making a mat of pulp with water on a moving screen. The mat is sized and filled for various pur-

poses.

Proteins have apparently been built up from amino acids and may be hydrolyzed to give these acids again. The process of digestion breaks apart the proteins to give amino acids which may be utilized by the body to form new tissue.

REVIEW QUESTIONS

1. Into what classes do we place sugars? What is the basis for this?

2. What happens to cane sugar during digestion? How can this

change be produced in the laboratory?

3. What compound represents the final digestion of starch? How can this change be brought about in the laboratory?

- 4. Can cellulose be digested in the body? Can it be converted to edible substances in the laboratory?
 - 5. What do we mean by corn sugar? How is it made?
 - 6. What is the source of dextrimaltose used in milk drinks?
- 7. Would you say that we pasteurize milk to keep it from souring? Explain.
- 8. Give a reason for thinking that starch and cellulose are

built up from similar "building blocks."

- 9. Trace the digestion of starch in the body.
- 10. What do we mean by an enzyme? Are these little animals and plants?
- 11. What disease is associated with the inability of a person to use dextrose as a body fuel? How is this difficulty usually overcome?
- 12. What are the following: pyroxylin; viscose; celanese; safety glass; guncotton; cellophane?
 - 13. How is wood pulp prepared? Describe the manufacture of

paper.

- 14. Would sugar serve as a complete food? Why?
- 15. From the chemical viewpoint why is a balanced diet necessary?
- 16. To what extent are the digestive processes for fats, carbohydrates, and proteins similar?

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VITAMINS. HORMONES. DRUGS

It has long been known that man and other animals cannot exist on fats, carbohydrates, and proteins alone. Just as plants need minerals so do animals. Their growth may be retarded, their bones and muscle structure stunted, by the complete absence of a mineral which normally occurs in the body in very minute amounts. Makers of iodized table salt have often called our attention to the value of iodine to keep our thyroid glands, and thus our bodies, healthy. There are reports concerning the necessity for very small amounts of cobalt in the food for certain farm animals. Calcium and phosphates are vitally necessary to form the calcium phosphate of which the bones are made. The blood contains iron though the total amount of this element present in the body at one time is probably little more than one tenth of an ounce. Common salt must be supplied at all times since the various parts of the body are continually bathed with a salt solution. To furnish our bodies with these many needed minerals we eat green vegetables. These are excellent sources of minerals. But frequently unwise cooks boil the minerals out of vegetables and throw away the water. Milk, too, is quite rich in minerals.

Observations over a long period of time have shown that still other chemicals must be present in the food we eat if the body is to function properly. The person who eats plenty of fruits, vegetables, meat, and milk will in no way suffer from the lack of these other substances. But a person whose diet is restricted to a very few things may show signs of physical failure and breakdown. Throughout history, before modern speed in transportation, sailors and explorers have been known to suffer scurvy and sometimes death from the absence of

fruits and vegetables. Poverty-stricken people have always been susceptible to skin diseases. These and other facts have all pointed toward additional physiological food requirements which are not shown by an ordinary analysis of foods.

VITAMINS

These special food materials have been classed as vitamins. We are bombarded with advertising matter which urges us to buy this food or that food because it contains the health-giving vitamins. We are almost led to believe that it is only through the purchase of these special preparations that we can expect to keep alive. As a matter of fact, most of us probably eat everything which we should eat unless we are hard hit by poverty, or are in an isolated location, or lose our appetite. Of course, it is well to pay attention to diet in order to insure the best possible health but there is little reason for most of us to spend extra money on pills or capsules when it is a lot more fun to eat good food. There are several of these vitamins which have been definitely isolated and they have been identified by means of a letter for the want of better names.

Vitamin A. The lack of the substance which we call vitamin A has been noted for more than 50 years. It was not until about 1913, however, that it was proved to be a food requirement. In its absence humans and animals are more subject to eye infections and are unable to adjust their eyes to see in dim light. This is called night blindness. Moreover, the general health of the body appears to be better when this vitamin A is present. It is found in milk products, yolks of eggs, liver, green-leaf vegetables, and in the yellow parts of plants such as carrots. Cod-liver oil and other fish-liver oils contain the vitamin in concentrated form. The yellow coloring matter of carrots is carotene and this is changed to the vitamin within the animal body. Because of this, carotene is frequently called provitamin A.

The chemical formula for the vitamin is C₂₀H₂₉OH. It is a highly unsaturated alcohol. The formula for carotene is

 $C_{40}H_{56}$ and it is a highly unsaturated hydrocarbon. Within the body this hydrocarbon is made to react with water and split into two parts:

$$C_{40}H_{56} + 2H_2O \rightarrow 2C_{20}H_{29}OH$$
 carotene Vitamin A

The chemist assigns this vitamin the following structure which was established by Paul Karrer, a chemist of Zürich.

Vitamin B₁. In the East Indies a great many of the natives live on a diet of rice. When polished rice was made available to them they used it and soon became stricken with a nervous disease known as beriberi. Later it was shown that the disease disappeared when the unpolished rice was again used. It was established that some food factor is present in the covering of the rice kernel. Other sources of this same food factor are whole-grain cereals, milk, eggs, tomatoes, liver, and grapes.

The identity of the vitamin contained in the rice polishings was established by R. R. Williams, a chemist for the Bell Telephone Company, who was stationed at one time in the Philippine Islands. He followed the problem through as a hobby in his spare time. As a result of his efforts the pure vitamin was isolated from natural sources and later it was made synthetically by him. It is now sold as "thiamin." He established its structural formula.

Vitamin B₂ (G). In milk there is a substance called *ribo-flavin* which seems to be essential for growth and general health. In Europe it is called vitamin B₂ but in America it is termed vitamin G. The structure was established by Karrer who synthesized it. He gives it the following formula:

Vitamin C. For hundreds of years the disease known as scurvy has been recognized among sailors, the length of whose voyages prevented the use of raw vegetables and fruits as foods. The suggestion was made two hundred years ago that vegetables were needed to prevent this disease. Within recent years the active vitamin material has been isolated and shown to be the same as an already known substance. It is named "ascorbic acid," or "cevitamic acid." Its formula is given.

It is made synthetically from a simple sugar. Heat and air together tend to destroy this compound and thus it is usually not present in cooked foods. However, some canned foods such as tomatoes retain the vitamin. A plentiful supply of vitamin C may be obtained if the diet includes such things as

oranges, grapefruit, lemons, tomatoes, and raw cabbage. The actual amount of the vitamin required appears to be much higher than in the case of vitamin B and efforts should be made to include as much of it as possible in the food.

There is additional evidence which indicates the need for vitamin C for general good health. Together with vitamin D

it helps to make better teeth.

Vitamin D. The disease known as rickets has affected innumerable American children, particularly those who live in dark cramped tenements. Rickets results when the body is unable to form proper bone tissue. Even in the presence of an abundance of calcium and phosphates the bones fail to develop. Long ago it was noticed that this disease appeared more frequently in the winter months and would disappear in the summer. By feeding cod-liver oil to children it has been possible to prevent the disease entirely. Further investigation has shown that sunlight or ultraviolet light from a special lamp will cause the disease to disappear and will also prevent it. A substance known as *ergosterol* which occurs in yeast is changed by ultraviolet light to viosterol which will prevent or cure rickets. It is thought that ergosterol also occurs in the skin and is converted by ultraviolet light, from the sun or lamp, to this same viosterol. Many foods are treated with ultraviolet light in order to increase their content of this substance. Such foods are said to be irradiated.

The fad for sun-tan is, in part at least, due to the idea that sunshine builds up the supply of this substance which has come to be called vitamin D. Sunshine is truly important but the careless exposure of the body to the rays of the sun may cause trouble far more serious than rickets. Actually, enough sunlight will fall upon the face and hands to care for most of the needs.

Vitamin E. This vitamin is called the reproductive vitamin since in its absence animals and humans become sterile and unable to have offspring. This substance occurs in certain vegetables such as lettuce and in the oil surrounding the germ of wheat, corn, and other grains. The pure vitamin has been

isolated as an oil and it has been made in the laboratory by Dr. Lee I. Smith at the University of Minnesota. Present knowledge indicates that its structure is:

Vitamin B₆ (pellagra preventative). The skin disease known as pellagra has been a scourge of certain southern sections for many years. Usually the persons affected have scant diet because they have no cash with which to buy food. The disease may be overcome by the free use of milk and lean meat together with eggs. A substance which is an active cure for pellagra has been isolated and found to be a compound related to nicotine. It is called nicotinic acid.

$$\begin{array}{c} H \\ \downarrow \\ C \\ H-C \\ \downarrow \\ C \\ C-C \\ OH \\ C-H \end{array}$$

The chemist cannot have all of the credit for the isolation and synthesis of the vitamins. He has been just one of the many groups including physiologists, biologists, and dieticians who have made definite contributions to this important study. In every case the progress of the research has depended upon feeding experiments involving animals such as rats. Foods which are rich in particular vitamins have been determined. From these, concentrated extracts of the vitamins are prepared. From these extracts the pure vitamin has been isolated. At this point the work of the chemist begins. He examines the compound, called the vitamin, in every chemical way in order to decide the elements which may be present and the structure of the

molecules. After he thinks he is sure of the structure he sets about to build up a molecule by chemical methods. Starting with a substance having a similar molecule or a molecule like a part of the vitamin molecule he adds groups to it or takes groups away from it in order to accomplish his purpose. When he is through, the rat-feeding experiments must be done over again in order to be sure that the synthetic compound has the same effect upon an animal as does the natural product. All in all, like much experimental work, it is a long drawn out process which requires knowledge, skill, patience and determination.

Vitamin K. Medical science has long been baffled by the fact that certain persons have blood which will not clot in the proper manner. This is of extreme importance in cases which involve surgery. A number of newborn children suffer in their first week because of hemorrhage. In young chicks the small blood vessels sometimes burst and produce a general condition of bleeding beneath the skin. It has been determined that a substance present in fish meal and in alfalfa will prevent this trouble in chicks if these are included in their food. Professor E. A. Doisy and his helpers at Saint Louis University succeeded in isolating this effective material during 1939. Its synthesis by them and others has since been reported. Its structure is written in the following manner:

The injection of this substance into the blood results in greatly accelerated clotting time. Its use will make many surgical operations safer. Present information indicates that its use will not benefit those suffering with inherited hemophilia. Administered to expectant mothers it appears to diminish the danger of hemorrhage in the child.

HORMONES

The chemical changes which take place within the body are not entirely controlled by enzymes, mineral salts, and vitamins as one may be led to believe by the earlier discussions. The body has its own system of regulation and a part of this is of a chemical nature. There are certain substances produced within the body and carried by the blood stream to other organs or tissues where they produce an activity. These substances are called hormones. They are produced by the glands of internal secretion, sometimes called the ductless glands. It is such a gland secretion which causes the male bird to be highly colored and full of song. Other secretions control the rate of growth. Hence it is obvious that improper gland control results in a dwarf or a giant. In a like manner the body is controlled during fear, anger, or other emotions. Already we have mentioned one such secretion, insulin, which enables the body to burn glucose as a fuel.

Thyroxin. Just beneath the muscles of the neck there is a gland called the thyroid and its secretion is called thyroxin. This gland controls the growth of both body and mind by supplying thyroxin to the blood. Another important part played by thyroxin is the control of the oxidation of fuel in the body tissues. The human body has been compared with a furnace and thyroxin is said to open up the draft so that the fires may burn rapidly. During good health the thyroid gland supplies the correct amount of thyroxin to keep the fires of the body going at the correct rate.

After considerable effort the chemical structure was established by C. R. Harrington of London as follows:

It may be recognized as an amino acid. Since it contains iodine it is necessary that a little iodine be consumed along with the food which we eat or with the water which we drink. The sale of iodized salt has been prompted because in some areas there is no natural iodine in the soil, or water. Some cities in this "goiter belt" add sodium iodide to the drinking water. This hormone is now manufactured synthetically for the use of physicians.

Adrenalin. When an animal or man is faced with a sudden fear such as when a car suddenly speeds out of a side road and you are not sure whether you can miss it or not, there is a secretion supplied to the blood from the adrenal glands in the back. This secretion called adrenalin causes the blood vessels to contract, the heart to speed up, and great blood pressure results. Glucose is also released into the blood from the liver so that the body is in condition to perform an immediate and extra heavy task. Furthermore, in the presence of adrenalin the blood clots much more easily than normally and thus bleeding is stopped in case of minor injury during a fight with an enemy.

Adrenalin was synthesized as early as 1908. It has the following structure:

It is used extensively in medical practice. It causes a failing heart to beat more firmly. It constricts the blood vessels around a point of injury or around a minor operation. It is injected along with novocaine around a tooth to be extracted. An unusual use is to relax the muscles of the breathing ducts in cases of asthma.

Sex Hormones. Within recent years a great amount of medical and chemical study has been given to the hormones that

influence sex characteristics. It has been proved that the sex glands secrete compounds which bring about the changes as the body nears maturity. The male hormone causes the growth of hair on the face and the enlargement of that portion of the larynx which lowers the pitch of a boy's voice. The female hormones bring about those changes which result in enlarged breasts and hair growth on the pubis, and in the armpits. There are two or more male hormones and possibly four or more female hormones. Each hormone plays also a particular part in the reproductive process.

Even though the sex hormones are important in the control of the sex processes they are not the primary substances responsible for this action. The master hormone, or group of hormones, is secreted by the anterior lobe of the pituitary gland and passes in the blood stream to the sex glands. There it stimulates these organs to produce either male or female hormones. These active substances from the pituitary are called *gonadotropic* hormones. That both types of hormones are produced by either sex is shown by the fact that the urine of the stallion contains more female hormone than does the urine of the pregnant mare, the next best source.

The chief male hormones are androsterone,

and testosterone,

The female hormones are theelin (oestrone),

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and pregnandiol,

Even a person not too well acquainted with chemistry can see that the formulas for these compounds are quite similar. It is certain that these substances act in a strictly chemical fashion, and, because of this, they and many other hormones are known as chemical regulators.

The field of hormones has hardly been scratched. At the

The field of hormones has hardly been scratched. At the present time it is one of the most active branches of chemistry as well as of physiology. Large numbers of workers are employed in the many investigations under way. The use of sex hormones in medical practice is becoming established. The relief from human suffering which the use of these hormones has brought about is truly remarkable. However, we still must rely upon animals and man for the source of supply. Someday the chemist will be able to synthesize these hormones and supply them in pure form free from any contaminating matter.

DRUGS

As far back in history as we may go we find that man has used various preparations to ease his pain and drive away his illness. We shall not attempt to trace the progress of medicine, but we may recall that early in the sixteenth century Paracelsus preached the idea that life is a chemical process. He was a teacher of medicine and he compelled his students to study a little chemistry. He also induced the alchemists to give up their search for gold and devote their efforts to the preparation of remedies. Since then the progress of chemistry in medicine has been very definite though sometimes quite slow. At the present time we have some remedies of a general nature such as "aspirin" which is called upon to help everything from a toothache to a case of "nerves." On the other hand there are some remedies which are specific for certain ailments. Thus "salvarsan" was made to combat syphilis and "sulfanilamide" is used to fight streptococcic infections.

nilamide" is used to fight streptococcic infections.

In general we may classify the majority of medicines into such groups as laxatives, pain easers, germ destroyers and inhibitors, narcotics, etc., but a complete list would become too

large. We shall attempt to consider a very few substances which represent real chemical achievement in medicine.

Aspirin. Because of well-planned and executed advertising the average person is acquainted with aspirin and its uses. This substance is one of many related compounds which possess the ability to relieve pain and reduce fever as well as ease rheumatic conditions. The substance from which all of these compounds are made is *salicylic acid*. The pure stuff is not so pleasant to take, however, as are many of its derivatives. Some of these derivatives are even more effective than is salicylic acid. Aspirin is *acetylsalicylic acid*:

It may be made by chemical changes from substances obtained from coal tar (benzene), and because of this it is classed as a "coal tar" medicine. Some persons, because of their chemical make-up, are unable to use aspirin. Others suffer from its overuse. From the enormous quantities of this material sold one might imagine that it is habit forming but such a notion is entirely without foundation.

In many cases of rheumatic pains and muscular soreness the physician may prescribe the use of *sodium salicylate*. This is the salt formed by neutralizing salicylic acid with sodium hydroxide. It is rapidly hydrolyzed in the stomach to give salicylic acid and many persons are not able to retain it on account of this. Just how the salicylates, including aspirin, are able to relieve pain is not understood.

It is quite interesting that the flavoring called oil of wintergreen is chemically related to aspirin. Produced by the union of salicylic acid with methyl alcohol it is *methyl salicylate*:

Phenacetin. Another type of pain relievers contain compounds made from *para-aminophenol:*

The most common of these is called *phenacetin*:

All of these preparations are used as headache tablets and to relieve fever. They actually do relieve these conditions but their use should be carefully controlled by a physician. In some people they have a pronounced action on the blood by the destruction of the red corpuscles. They depress the heart action also. In many diseases this action would be quite dangerous.

Amytal. It is frequently necessary to administer a powerful and effective pain reliever. For this there is a group of compounds which may be made from barbituric acid. All of these tend to relieve pain, quiet the nerves, and produce sleep. This last property, that of producing sleep, has caused many persons to use these substances. One of the best known of these is amytal:

$$H-N-C=O$$
 $O=C$
 C_5H_{11}
 C_2H_5
 $H-N-C=O$

Other such compounds are known as "neonal," "ipral," "pentobarbital," "luminal" and "dial." All of these are the same except for the two hydrocarbon radicals (C₅H₁₁ and C₂H₅)

which may be replaced by others.

All of these compounds are effective sedatives and hypnotics, and are used in hysteria, insomnia, epilepsy, and in mental disturbances. They are frequently used together with the salicylates for the relief of neuralgic pain. With sodium hydroxide these compounds form sodium salts since one of the hydrogen atoms attached to nitrogen (H-N) behaves like the hydrogen in acids. These salts are more soluble and give more rapid action than do the original substances.

Under the care of a physician these substances are relatively

safe but their careless use may result in collapse.

Pep Pills. Within the past few years there has been a tremendous increase in the consumption of drugs which prevent sleep. Possibly it is because of the strain of modern living. Further, we find that great sales of these drugs occur near colleges and universities during examination periods. One of the most popular substances used for this purpose is *benze-drine*:

Experimenters are watching it to discover if its use is dangerous. They know that it does cause restlessness and encourages the dangerous practice of "burning the candle at both ends."

Ephedrine. The many thousands of persons who suffer from sinus infections and asthma are grateful for *ephedrine*. By its use the swollen membranes of the sinus may be shrunk to normal size and thus it results in relief from intense pain. Its effect upon the muscles as well as upon the nervous system helps materially in the prevention of attacks of asthma. Most of the compound used is prepared from a Chinese herb, *ma buang*. Chemically it is much like adrenalin which we would expect from its structure.

Methods for its synthesis have been discovered but as yet we are dependent upon China for our supply.

450 VITAMINS. HORMONES. DRUGS

Cocaine. The use of cocaine has relieved much suffering because of its action as a local anesthetic. This material which occurs naturally in the leaves of a certain coca tree also has many effects upon the human body which are detrimental. One of the greatest objections to it is the fact that its use is habit forming. The chemical structure of this compound has been determined after years of experimentation. It may be seen to be a nitrogen-containing substance.

Hundreds of experiments with similarly constituted compounds have revealed the fact that it is the arrangement of atoms found within the dotted rectangle which contributes the anesthetic properties to cocaine. A number of new compounds containing this or a similar grouping of atoms have been made and they all have anesthetic action when injected into animals. The most successful of these is known as *procaine* or *novocaine*:

Novocaine is used successfully in many minor operations and is the chief substance injected around a tooth which is to be

pulled.

The investigations which resulted in the discovery of novocaine are typical of things which are constantly being done by chemists. Some persons think that these things are done because of an unsatisfied curiosity on the part of the chemist and in part they are right. But chemists also look on it as the performance of a duty to mankind.

Chaulmoogra Oil. There are many medicines which have been used for centuries because someone at sometime discovered that chewing the leaves of a certain tree or shrub would relieve a pain or cure an illness. The use of quinine to combat malaria is an outstanding example of this. Another is *chaulmoogra oil* which is used in the treatment of leprosy. In certain tropical countries of the Far East the natives have used this oil to rub on their leprosy wounds and have also taken it by mouth. Drinking the oil caused nausea and intense suffering. A native superstition was to the effect that the patient would get well if he could survive the treatment.

At about the beginning of the present century a study was begun for the purpose of finding out the chemical nature of chaulmoogra oil. Much has been accomplished by many experimenters. The oil has been treated with caustic soda and converted into a soap (natural oils are esters). Water solutions of this soap have been injected under the skin with some success. Another worker treated the oil with sulfuric acid and ethyl alcohol. This produced a compound which could be injected into the muscles. Remarkable results have come from its use.

These studies have resulted in the cure of many lepers. But the real advance in their treatment is just beginning. The true chemical nature of the effective part of chaulmoogra oil is now known. Other compounds by the score have been made and they are being tried. By changing a group of atoms in one part of the molecule the chemist is able to remove some of the poisonous effect of the natural oil, and, by adding a group of atoms in another part of the molecule, he is able to increase its action upon the germ of the disease. The effective part of the oil is the acid of the ester and is known as chaulmoogric acid:

It has been shown definitely that it is the ring in the molecule which has the particular effect wanted. By making a

molecule with the acid (—C—OH) group nearer to the ring chemists have improved its medicinal value.

At the present time it seems quite probable that leprosy will become a rare disease wherever treatment may be given. Many infected countries have already felt the effect of the research and are beginning to do away with their isolation colonies. The chemists together with the daring physicians who have made this possible cannot be praised too highly. No doubt they have started to wipe out a pestilence which has harassed the human race for more than 7000 years.

Sulfanilamide. In 1935, announcement was made of the successful use of *sulfanilamide* in the treatment of blood poisoning. Since that time it has been tried in all sorts of cases involving infection and contagious diseases. Hardly a month goes by without the addition of another disease to the list of those it helps to combat. Even in this day of wonders when no one is surprised at any new device which may come out we must stand in awe of the miraculous action of this drug. We must not consider it as a lucky accident, however. It came from a long series of experiments which were planned for the purpose. The compounds used at the beginning of these experiments have been known for thirty years and something of their action on bacteria has been known for much of this time. Those chemists who carried out the investigation fol-

lowed the usual procedure of making new compounds with molecules a little different from the ones last tried. They were finally able to hit upon the chemical groups which were essential. These were brought together in the same molecule and sulfanilamide was the result. Its structure is relatively simple:

This drug appears to retard the normal growth of the disease bacteria and thus gives the body a chance to kill them off. This, of course, calls for a relatively healthy body. It naturally follows that the drug will not be effective in all cases. Its use is not without danger. When used in large amounts, as is sometimes necessary, it causes the destruction of the blood cells. If certain foods or other medicinals such as laxatives are used along with sulfanilamide the results may become dangerous because of upset body conditions. It must be borne in mind that sulfanilamide should be used only under the direct supervision of a physician.

Sulfapyridine. The constant desire for a better product has resulted in the manufacture and testing of hundreds of derivatives of sulfanilamide. Many of these have been proved to be worthless and many others are a little less effective than sulfanilamide itself. Some are too violently poisonous to be considered. However, one product, called *sulfapyridine*, seems destined to revolutionize the treatment of pneumonia. Some physicians who have been experimenting with this drug have gone so far as to predict the end of deaths due to this disease. When it is remembered that pneumonia stands near the head of the list of diseases which cause death this prediction is almost unbelievable.

The chemical similarity of sulfapyridine to sulfanilamide is easily seen from its formula:

It is too early as yet to know very much about this new drug. However, it is known that all of the care necessary in the use of sulfanilamide must also be observed with sulfapyridine. Because of the dangerous nature of pneumonia, the patient is already in a critical condition and thus it becomes far more urgent that extreme care be used. Already the clinical methods have been standardized enough to release the drug for general medical practice.

The War on Syphilis. This chapter which deals with the usefulness of chemistry in the production of medicines would be incomplete without some mention of the part which chemistry has taken and will continue to take in the fight on syphilis. Because of government and medical public health activity the secretiveness connected with this widespread disease is fast disappearing, and thousands of infected persons are receiving treatment at the hands of competent physicians.

It was about the beginning of the present century that organic compounds containing arsenic were first used in experimental investigations. Most of these tests were made upon animals such as apes, rabbits, and rats. Those compounds which showed promise were carefully studied with regard to their action on the germs and their effect on the animal. New molecules were built and similar experiments were conducted over several years. The great German chemist, Ehrlich, made possible the use of an acceptable compound in 1910. This he called "Salvarsan" and it bore the number "606" in his records. We

do not know how many separate compounds had been tried in his laboratory but from the number assigned to this substance it must have been large.

The investigation did not stop here with apparent victory. Other compounds were made. There was the constant effort to decrease the poisonous effect of the drug on the body as well as the tendency of these compounds to affect the vision. Ehrlich was able to produce a much more desirable compound called *neoarsphenamine* with the following structure:

There are still other such compounds which can be used and many workers are making additional ones. In every case the new compound must be used in actual tests but the work has progressed to the extent that the chemist can usually predict the action of the new material before it has been tried. The work has come a long way since 1900 and there is reason to believe that syphilis, too, will before long give way before the combined assault of chemistry and medicine.

SUMMARY

The vitamins are compounds which appear to behave as body catalysts. Their presence is necessary for proper health. They and their functions are detected by feeding experiments using controlled diets. Present information confirms the presence of eight such materials which are listed as vitamins A, B₁, B₂, B₆, C, D, E, and K.

Certain glands of the body secrete regulating fluids known as hormones. These regulate growth, development, mentality,

and health. As with vitamins, many of these have been made in the laboratory by synthetic methods.

Drugs and remedies are best designed to fit into the chemistry of the body though some have an action which has not been explained. One compound which is applied with success brings forth other similarly constituted substances which as a rule have similar action. The physiological behavior of a drug appears to be a function of its molecular structure.

New developments are being made in the field of specific drugs which attack particular diseases. This has resulted from close co-operation between synthetic chemistry and medicine

along with the related sciences of disease.

REVIEW QUESTIONS

- 1. List the vitamins together with the effects produced by their absence.
- 2. In what respect do vitamins differ from hormones, both as to source and action?
- 3. Why should care be used in taking the common pain relieving drugs?

4. What do we mean by specific drugs?

5. Look up recent popular articles concerning sulfanilamide and sulfapyridine. List some of their uses.

6. What is the present status of the leper colony?

7. What governmental aid is being given to the war on syphilis?

8. Why do most states regulate the sale of compounds involving barbituric acid?

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RESEARCH—MOTHER OF PROGRESS

We have come to the final chapter in this survey of chemistry. Through all of the preceding pages we have tried to show that chemistry is not only a useful daily tool, but that it is also a tremendous factor in the development of American business industry and exerts a powerful force upon the destiny of men. In our discussion of chemistry we have chosen topics of universal interest because these apply not only to every person who reads this book but to everyone who lives, breathes, and enjoys modern society. Of course, we could not by any means tell the whole story. In any book there is a limitation upon the amount of material which may be presented. However, the reader may now have some conception of the contribution which chemistry has made and which it may continue to make in the future. This contribution never has been, and never will be, an accidental one. It is true that there have been a few accidental discoveries, unexpected by the researcher who made them, but even these usually came out of long experimenting on something else. But on the whole the results to which chemistry can point so proudly have been obtained because of planned investigations. Such planned investigation is called research.

Only a few years ago our industries were concerned chiefly with the natural materials which man has known for centuries. The fibers for our clothing and other textiles came from sheep, silkworms, and plants such as cotton and flax. Considerable attention was also given to the production of other such natural materials as hides, bone, ivory, saps of trees, and anything else which nature had processed and for which man

had found a use. The materials of construction, stone from quarry and field and wood from the forest, with which were built homes and factories, were the same as our forefathers had used. The clothing worn by people was the same sort of stuff as men had worn for hundreds of years. Even the soap used in laundries and in the home had not been materially improved for generations. It is true that men had improved the mechanical methods of making articles from nature's materials. But more than that they had done little.

Within the past quarter of a century, however, the entire business world has taken a wholly new attitude toward the raw materials which nature has supplied us. No longer do we praise the "natural" and scorn the "synthetic" product. No longer do men limit their inventive ideas to new ways to package the old goods. Now they try to take material which cannot itself be used and transform it through chemistry to new and unheard-of things which people can use. After these new articles are produced it is up to the sales forces to lure people to want them, buy them, and use them. Our modern commerce is full of such commodities. Some of them you know. For example, we have: antifreeze for our cars which is produced from waste oil refinery gas; synthetic methyl alcohol from coal and water; ammonia for the manufacture of fertilizers and explosives from water and air; modern plastics such as "bakelite" from coal tar, ammonia, and methyl alcohol; rayon and cellulose film such as cellophane from cotton and wood; material to prevent the knock in an automobile engine made possible because of bromine in sea water; and synthetic rubber of high quality from limestone, coal, water, and salt.

No one could foresee the far-reaching effect of the discovery of any one of these new products. It is quite probable that no one really saw that they were being discovered. It all came about so slowly. The first facts leading to these things were discovered many years ago by laboratory workers who were trying to investigate the properties of matter, doing what is called "pure" research. In the years which followed there were additional facts brought to light by still other workers. It

was upon such a foundation that the investigations of recent times began. Slowly the facts were pieced together, and someone, with the ability to see usefulness in the uncommon, found how to make a new material. He showed that it could be used to make something which would fill a human need. Thus it is that the inventor in modern times does not have to work with the old materials; he has access to thousands of the new. With these he gets new inspirations.

This business of finding out about what things are chemically as well as what they will do and what can be made from them as chemical substances is studied with profound practical interest by manufacturing industries. During 1938 the industries of the United States spent more than \$250,000,000 for research. This was not limited to a few concerns but included nearly 1800 laboratories. Likewise it did not include the vast amount done by college and university workers. A great amount of the total was spent in the development of new raw materials. However, every manufacturer must protect his own product at all times. One way of doing this is through research. If some new use can be found for his product he should be the one to find it if he can. And if a product can be found which can force his off the market, he had better be the one who finds it. Thus research is partly for protection and partly for development.

An example of what can happen is found in the wood distillation industry. A few years ago the industry which makes charcoal was also producing wood alcohol, acetone, and acetic acid by somewhat wasteful and costly methods. They had nothing to worry about because all of the wood alcohol consumed by other industries had to be purchased from them at their price. Suddenly the entire wood distillation business was caught "flat-footed" when it was announced that methyl alcohol could be produced synthetically at a fraction of the cost of their product. The investment in wood distillation equipment in this country was something like \$35,000,000. Almost overnight its value was considerably reduced. They did not go out of business, however, because the prohibition

laws then in effect stipulated that "wood spirits" must be used to denature grain alcohol in order to avoid the high tax.

This allowed a period of a few years for the industry to put their house in order. They began research and found that they could cut costs here and there in their processes. They sought new markets for their products and are now seeking new uses for the things which they make. In the meantime, they have seen the chemists produce acetone and acetic acid by synthetic processes. However, thanks to their research, they are still in business for the time being and may not be done for at all if they keep up their research. Of course, they are helped to a considerable extent by the fact that they produce charcoal which still finds a sale.

There are hundreds of outstanding examples of firms that have prospered through research. Their achievements have placed the United States at the top in industrial progress. The ramifications of modern industrial research are illustrated in the histories of certain products. Some of these have recently been brought together. An instance is to be found in *Industrial and*

Engineering Chemistry, May 1939.

Taking Pictures. The man who founded the Eastman Kodak Company learned the art of taking pictures in 1877. He realized that his art, like the other arts, had a scientific foundation and that chemistry was involved in the process. Hence he spent much time with chemical textbooks. His hobby, with him, became almost a passion. There were so many obvious improvements to be made and almost from the first he could see them. The "portable" camera outfit of those days included a cumbersome camera, a light-proof tent, bottles of solutions into which the photographic plate had to be dipped just before exposure, and other solutions for the development of the picture immediately after exposure.

By 1880 he had done a lot of experimenting and was in the business of making photographic plates to be used dry. All plates used at that time were of glass and Eastman schemed to decrease the weight and bulk. Research (investigation) demonstrated that the photographic coating could be applied to a

strip of paper instead of to glass. This was done. But further research, together with actual tryouts, showed this to be unsatisfactory. His investigation then turned to cellulose nitrate. Eastman realized that he was not enough of a chemist to solve the problem. In 1886 he hired a chemist to work on the coating of cellulose nitrate film with photographic material. It took three years to solve the problem but together they produced a transparent film which could be sold in the form of a roll. So far as is known this was one of the first research chemists to be employed by an American firm.

Other experiments and additional workers followed and these brought about modifications of the camera and apparatus to be used for amateur developing and printing. Soon afterward the motion-picture film was devised. As the industry gained in momentum it became necessary to investigate the chemistry of nitrocellulose products. This was followed by a study of cellulose acetate for safety film in home movie sets. Before they got very far the investigations took them into the field of glass and the construction of lenses. Because they needed a large amount of special paper for printing pictures they had to create a new process of papermaking. Large amounts of chemicals of known purity were required which they were forced to manufacture.

Out of such an organization is sure to come a lot of knowledge. Their chemists and other research workers became experts in their fields. From the knowledge of cellulose acetate gained through study of safety film the company was able to start the manufacture of cellulose acetate rayon. This lowered the cost of their film but it also placed them as one of the largest acetate rayon producers in the world. For the same reason they supply much of the cellulose acetate to be used as the middle strip in laminated safety glass. Their chemical manufacturing department now offers more than 3000 organic chemicals for sale. Many of these cannot be obtained elsewhere. This branch of the picture-taking business has been a remarkable aid to research chemists all over the country.

This industry was founded and built upon research. Since

1886 the research force has been expanded to about 500 persons. However, these are not all chemists. They must cover all phases of the industry and include such fields as raw materials,

processing, and use of the products.

Antifreeze for Cars. More than fifteen years ago a firm which manufactured and sold acetylene hit upon the idea of producing it from petroleum. If you recall we have mentioned the preparation of acetylene from calcium carbide. By cracking the petroleum under certain conditions their research workers were able to produce acetylene and their plan was seemingly successful. However, in the purification of the acetylene they discovered that considerable ethylene was also produced. So much ethylene was produced that they had to find a use for it. To throw it away would make the process too expensive. They could not leave it in with the acetylene.

These research workers knew that ethylene could be converted to a compound known as ethylene glycol (Chapter 17) but they did not know how to do this on a large scale. When once obtained, ethylene glycol could be used as a substitute for glycerin in nitroglycerin. They began their investigation with such use in view. The chemical change neces-

sary is not very complex.

However, all methods used up to that time by other laboratory workers had failed to give satisfactory results.

It was not long after the new research started that the persons in charge began to report success. They were so positive of their results that the manufacturers began to produce ethylene glycol in large quantities. However, instead of offering it for sale to the makers of nitroglycerin and dynamite they created a new market at a higher price. They sold it to automobile owners as an antifreeze.

Just as soon as large quantities of ethylene glycol became available other investigations of its chemical properties were begun. They wanted to know if any useful substances could be produced from it by chemical action. More than a dozen such compounds have been produced and they find a sale as solvents. One of these, diethylene glycol, is used in a nationally known brand of cigarettes to keep the tobacco moist. Another, called butyl cellosolve, is used in a number of window cleaning fluids.

As a result of the work on ethylene some of the major oil companies began to investigate the gases produced in their own cracking plants. They found fairly large amounts of the gas propylene.

By means of simple chemical changes it was possible for them to produce isopropyl alcohol from this gas.

While this alcohol is an important solvent it finds still greater application in the production of acetone. A catalytic process is used to remove two hydrogen atoms from each molecule of the alcohol.

Acetone is used in extremely large amounts as a solvent for lacquers. It is also used as a solvent for removing fingernail polish from the nails.

When isopropyl alcohol is heated with sulfuric acid under the proper conditions it yields isopropyl ether.

Further investigation showed that isopropyl ether could be used in automobiles for fuel and that it has remarkable anti-knock qualities. Because of this, military airplanes now use some gasoline with an octane number of 100.

Ethyl Gasoline. During the time that various industrial concerns were doing research on the ways to use ethylene a major change took place in the field of automobile fuels. The antiknock catalyst, lead tetraethyl, was discovered and developed. Like other important discoveries it required years of research and the expenditure of large sums of money. The promoters claim to have spent \$3,000,000 on this discovery. After they had all of the detail work cared for and they were sure of their product it became necessary for them to look about for their source of raw materials.

One substance used in the manufacture of lead tetraethyl is ethyl chloride. Ethylene proved to be the ideal starting material from which to make this since it gives ethyl chloride at once when treated with hydrogen chloride.

This opened up a new outlet for ethylene at once but created a tremendous demand for hydrogen chloride. It may be recalled that hydrogen and chlorine unite readily to produce this. Another substance necessary for the satisfactory production of lead tetraethyl is sodium. To get this they pass electricity through melted sodium chloride (salt). At the negative electrode they get sodium and at the positive electrode they get chlorine. The large-scale application of this process required tremendous amounts of research before it was satisfactory.

The use of lead tetraethyl in automobiles was still not a reality. In the gasoline along with the lead tetraethyl, it is necessary to put ethylene dibromide. The bromine and the lead combine during the combustion in the cylinder. This renders the lead harmless to the engine and to people. There was no source of bromine which could begin to supply the demand the manufacturers hoped to create. They had to go out and find a new supply. Somewhere they read that the water in the ocean contains 67 pounds of bromine in a million pounds of water. They figured there was a lot of bromine available in the ocean and they went after it. Getting it was another giant problem. Again research brought the answer, but it took money and time. Now they take 1,500,000 pounds of bromine from the ocean each month.

This has been a typical story of research but still it is not ended. The corporation which developed lead tetraethyl believes in continued research as the key to progress. They now expend more than a third of a million dollars each year just to pay the men and women who do their research.

Mellon Institute. In 1907, Robert Kennedy Duncan, then professor of industrial chemistry at the University of Kansas, established a system of cooperation between the university and various industries. The University had able chemists on the staff and had considerable research facilities. Duncan, who had traveled extensively in this country and in Europe, was convinced that American industry suffered from confusion and waste so far as chemical information and guidance were concerned. He proposed that the universities could help to correct this condition.

The first of these cooperative projects had to do with a

study of the chemistry of laundering. A definite agreement was drawn up concerning the financial aid to be donated by the manufacturer of laundry material, the supervision of the project by the University, and the use of any discoveries. It is of considerable importance to note that all discoveries were to become the property of the donating manufacturer and that proper financial recognition was to be given to the worker making the discovery.

This plan was found to be satisfactory both to the cooperating industry and to the University. Soon there were other "Industrial Fellowships" at the University of Kansas. They covered such widely separated fields as bread making, casein production from buttermilk, constituents of petroleum, enamel coatings for steel, portland cement, finishes for wood, and the

production of adrenalin.

The work being done by Duncan came to the attention of the late Andrew Mellon. So impressed was he with the possibilities of cooperative university and industrial research that he and his brother brought about the formation of a department of industrial research at the University of Pittsburgh in 1911. They furnished the funds for a small building and under the guidance of Professor Duncan they set up a system of industrial fellowships. These were exceedingly successful from the very beginning. In 1915 the Mellon family built a large building to house the project which in the meantime had taken on the name of Mellon Institute.

From the research done at Mellon Institute there have come several industries which did not exist before. Untold improvements have come to many already existing firms. The story of ethylene glycol for antifreeze is a chapter taken from Mellon Institute. Such success has caused the rapid growth of the institute and in 1937 it moved into a building which cost the Mellon family many millions of dollars. Within the building there is every means for conducting research. During 1938 there were 86 fellowships in operation, and the institute employed altogether more than 250 trained workers. Many of these have been continuous for five, ten, fifteen or even twenty

years. The institute spent more than a million dollars on pure and applied research during that year. It is remarkable that even though Robert Kennedy Duncan died in 1914, his original ideas have prevailed and the fellowships operate along the lines which he suggested.

The projects accepted for study are not concerned with chemistry alone. We find them investigating such things as food for children, heat insulation, fireproofing materials, coffee making, meat tenderization, air purification, and treatment for pneumonia. All of these are allied with chemistry and ac-

tually represent chemistry at work.

Other Research Foundations. The usefulness of industrial fellowships and other means of cooperation between industry and the universities or research organizations has been recognized all over the country. Several research foundations have been organized and are carrying on important investigations. Among these are: Battelle Memorial Institute in Columbus, Ohio; Purdue Research Foundation at Purdue University in Indiana; Armour Research Foundation at Armour Institute in Chicago; Ohio State University Research Foundation; and the Institute of Paper Chemistry at Appleton, Wisconsin. In the main, all of these follow the general plan of the Mellon Institute though they each adapt it to their own situations. The aims of all of them are the same; they desire to cooperate with industry to the benefit of the industry and those taking part in the research.

Federal Research. The United States Government supports the largest research organization in the world. Under the various bureaus we find scientists working with foods and drugs, use of farm crops, fertilizer materials, national defense, and standards of production. All of these are directly concerned with chemistry. However, there are still other bureaus which conduct research and which employ chemists and chemical methods to a considerable extent. The various branches and fields of endeavor are entirely too many to attempt description here.

Chemicals from Farm Crops. Federal research is attempt-

ing to find an answer to the agelong farm problem. The farmer suffers too much from swollen markets, uncertain weather, and insects. His business is too uncertain. If his surplus crops can be harvested as chemical substances he may stand a chance of a higher average income. Already government research is getting results. The citrus fruit growers find that their surplus and cull fruit is being used to produce *citric acid* which finds ready sale as a chemical. An important compound, *furfural*, is being made from waste oat hulls by a manufacturer of breakfast food. Chemical cellulose is being made from the crushed refuse stalks of sugar cane. This alone may result in a tremendous conservation of forest timber. A recent process for the production of a high grade of starch from sweet potatoes may help to solve a part of the crop problem in the south.

An interesting turn of governmental research has had to do with the establishment of a laboratory for the investigation of soy beans. This bean, introduced from the Orient, is a source of many valuable substances. Already it is furnishing oils for paints, plastics, proteins, and waterproof glue. The possibili-

ties appear to be many.

Quite recently the Congress of the United States has authorized the establishment of four Regional Laboratories to investigate farm crops. These are located at, or near, New Orleans, Louisiana; Peoria, Illinois; San Francisco, California; and Philadelphia, Pennsylvania. Construction of these laboratories has been started and the staff is being slowly organized. By the time they are ready for operation there will be about 500 chemists ready to begin their duties. Whether these laboratories will furnish a satisfactory answer to the farm problem remains to be seen, but we may safely predict that out of them will come a number of things which will be of great benefit. Wherever research is used it gets results. It has a record of more than paying its way.

Biological Research. Throughout this book we have taken advantage of every opportunity to mention the part which chemistry is taking in research in the fields of biology and medicine. Centuries ago the alchemists and others sought a

philosopher's stone which was supposed to be an elixir of life. They sought supernatural methods whereby they could hold onto the threads of life just a little longer. Most people still have those same desires. However, the methods of obtaining longer life have changed. No longer is the answer expected through dealing with the supernatural. We have attained a certain measure of success through the utilization of knowledge. This knowledge has been gained through many years of difficult and complex research. Much of it has been done by biologists and physiologists who have been thoroughly trained in chemistry.

The bodies of men and animals contain the most interesting and complex chemical laboratories that we know anything about. All of the raw materials used in these laboratories are taken in through the mouth and must be sorted and classified within the body itself. These sorted materials are then supplied to the proper organs where they may be utilized. Upsets in the mechanism may be expected. The causes of these upsets and the remedies for them are learned only through research. We have pointed out that these are sometimes due to a lack of proper food and sometimes due to the failure of a part of the body to supply the proper hormones. The entire field of medicine and medical practice is concerned with this laboratory in the body. Much research has been done and a remarkable amount of success has been attained. However, the field has been only touched and far more remains undone than has ever been accomplished.

The research has not been limited to men. We have mentioned the investigations concerning fertilizers for plants and farm crops. These have increased our national income and have conserved our resources. However, the work on the diseases of farm animals must not be overlooked. Biochemical methods have proved valuable in this. Such research is extremely important and upon it hangs a vital part of our national economy. Chemistry is securely tied to all types of research which deal with life processes. It is thus a service science and through such service it attains its greatest goal.

Scientific Societies. There is an important factor in scientific research which is not apparent to one outside of science * work. This is the contribution of the various scientific societies. There are many of these in all countries and they are devoted to the various fields of science. Among these societies are found those for chemists, biochemists, biologists, physiologists, physicists, engineers, etc. Most of them promote publications which are made up chiefly of scientific reports. These reports are usually in the form of carefully worded discussions accompanied by descriptions of experimental methods and data. Thus they serve as historical documents. Since they are usually indexed and cross indexed both by title and author they are of inestimable value to other laboratory workers. Before any type of research reaches the laboratory stage it is necessary that all possible publications be searched to see what has already been done. Without the scientific publications there would be endless repetition of laboratory work and progress would be exceedingly slow.

The largest organization of chemists in the world is the American Chemical Society. It was founded as an outgrowth of a group of chemists who visited the grave of Joseph Priestley in Pennsylvania in 1874 in celebration of his discovery of exygen one hundred years earlier. On April 6, 1876, the American Chemical Society held its first meeting in New York. It is a striking coincidence that this date was the two hundredth anniversary of the death of John Winthrop, Jr., who established the first chemical industry in the American Colonies.

From the small group of 35 men and women who formed the first organization, the American Chemical Society has grown to a giant. It now has more than 25,000 members and is still growing rapidly in spite of more rigid requirements for membership. Its activities include every branch of the science. Its annual budget amounts to about \$600,000. In order to further its aims it holds two general meetings each year in various parts of the country. Also, it fosters almost a hundred local sections located wherever there are enough chemists to justify the effort.

One of the chief functions of the American Chemical Society is the publication of its journals. Of these there are three:

(1) The Journal of the American Chemical Society publishes purely scientific articles based upon data obtained by experiment. The articles are contributed by workers all over the country and sometimes from foreign countries. Before being accepted for publication the articles must be read by experts in the particular field and given their approval as worthy.

(2) a. Industrial and Engineering Chemistry is published primarily for those connected with industry but includes much of vital interest to non-chemists. It deals with the

progress of chemistry at work.

b. A second section of the above publication is sent to all members of the society and is called the *News Edition*. It carries all the news of the official society and serves to keep the members informed concerning their organization. There are in it some articles of general interest.

c. The Analytical Edition is a third section of Industrial and Engineering Chemistry. It is entirely devoted to analytical methods of chemistry. These methods have a great value in the control and standardization of processes and

products.

(3) Chemical Abstracts is just what its name implies. During 1938 this publication carried more than 65,000 short abstracts of chemical and other scientific articles which were published in more than 1500 journals all over the world. These abstracts carry the name, volume, page, and year of the journal in which the original article may be found. There is frequently enough information given in the abstract to make it unnecessary to seek the original journal. To further aid research workers these abstracts are carefully indexed according to an easily understandable system.

Future Progress. In the light of the present we can only predict continued progress in chemistry. We are no longer surprised by any new discoveries because they have become so commonplace; we rather look forward to them and expect

them. There are yet uncountable unanswered problems and during the seeking for an answer many more problems will be brought to light. It has become to the chemists a great and absorbing game. Those on the sidelines need to know where the goals are and some of the rules. It is hoped that this book has made its contribution to this end.

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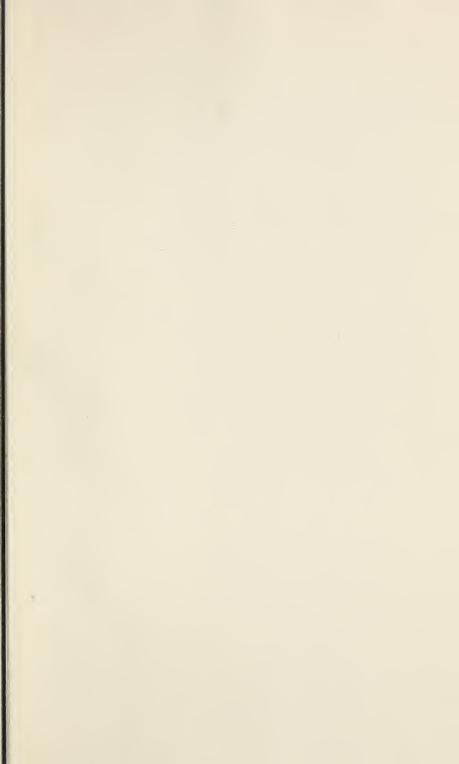
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